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**INTRODUCTION TO STATISTICAL MECHANICS
FOR STUDENTS OF PHYSICS AND
PHYSICAL CHEMISTRY**

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INTRODUCTION TO STATISTICAL
MECHANICS FOR STUDENTS
OF PHYSICS AND PHYSICAL
CHEMISTRY

BY

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FOREWORD

PHYSICO-CHEMICAL science regards the spatial universe as filled with a vast multitude of moving "elements" which possess both particulate and wave-like characters—the "wavicles" of Eddington. The only way to render this elusive and protean microcosmos amenable to mathematical calculation, and to interpret physical measurement, is to deal in terms of probabilities, to employ the statistical method. The macroscopic world of sense and the measurements based thereon possess the validity characteristic of the averages of an actuarial estimate. The statistical method is therefore of profound importance. It dominates the whole of modern science. Combined with the generalised principles of dynamics and the quantum theory it has produced statistical mechanics and "quantum statistics." These are not special branches of science peculiar to the needs of a few lonely mathematicians. The simple truth is that they constitute the fundamental basis of modern physical science. But another simple truth, though a painful one, is that they involve a severe discipline for the untutored human mind.

Fortunately, Professor Rice has now come to tutor our minds and bring consolation to our hearts. This book of his is a first-rate one, for which all serious students of chemistry and physics will owe him a deep and lasting debt of gratitude. He has explained and expounded the principles of statistical mechanics and quantum statistics with extreme lucidity. In the earlier portions of the book the general principles of probability and statistics are developed and applied to the solution of many important problems. Then the concepts of the quantum theory are introduced, and finally the generalised principles of dynamics. The most recent advances associated with the names of Bose, Einstein, Fermi and Dirac are dealt with in an important appendix. In excellent appendices to many of the chapters the author

succeeds admirably in removing the mathematical difficulties inherent in parts of the reasoning. I would particularly and very warmly commend this book to the attention of students of physical chemistry—it needs no recommendation to students of physics. Subjects such as chemical equilibria in gas reactions, the specific heats of gases and solids, the entropy of a perfect gas, the Nernst heat theorem, the chemical constants, the theory of the atom, the Einstein-Smoluchowsky theory of density fluctuations and collision-formulæ and chemical kinetics are all fully and clearly explained. Indeed, I will without hesitation make the two following assertions : (1) every student of physical chemistry must read the book ; (2) no student of physical chemistry familiar with the calculus will experience any serious difficulty in mastering its contents.

I make these assertions because I believe this book is destined to exert a great influence on the training of the present generation of chemists and physicists. As the title indicates, Professor Rice has had in view—and for that we cannot be too profoundly thankful—the needs of chemists as well as physicists. He has certainly succeeded in his object. But he has done so without any slurring over or evasion of difficulties. Throughout the work the treatment is thorough and complete. I would specially commend to the attention of chemists (and physicists) the two chapters which deal in a most clear and original manner with the second law of thermodynamics. The light which this statistical analysis of the microcosmos throws on one of the greatest—if not the greatest—of the experiential generalisations of the macrocosmos constitutes, to my mind, one of the great triumphs of the human mind. Seldom, if ever, has it been set forth with such masterly lucidity and logic.

This book is clearly the fruit of many years of study and thought. I wish it many years of prosperous and beneficent influence.

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PREFACE

THE aim and scope of this book is indicated in the introductory chapter. The author is not blind to the fact that the student he had in mind when he wrote it is not going to read some parts of it without a serious mental effort ; the necessarily mathematical form of the arguments entails that result. But he feels certain that any student with the average mathematical equipment acquired in the first two years of a University science course will not find it impossible to follow the details of the treatment, and as much assistance as possible is provided in explanatory appendices, in verbal interpretation and illustration. In the proofs no steps are omitted. On that account the content of subjects dealt with has had to be restricted ; otherwise the book would have grown to a length unsuitable for the type of reader whom it is intended to assist. The problems treated are concerned with systems in statistical equilibrium, although a short appendix refers to the subject of collision-frequency in gases and its bearing on chemical reactions.

The author's best thanks are due to Dr. A. McKeown and Mr. E. A. Stewardson, both of Liverpool University, for helpful advice and criticism, and to the former for reading the proofs.

J. RICE.

UNIVERSITY OF LIVERPOOL,
October, 1929.

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INTRODUCTION TO STATISTICAL MECHANICS FOR STUDENTS OF PHYSICS AND PHYSICAL CHEMISTRY

INTRODUCTION

THE experimental data which have acted as a guide to the discovery of the laws of physics and chemistry have been in the main derived from careful observation of the behaviour of very limited portions of matter deliberately and skilfully placed by the experimenter in artificial surroundings. The purpose of such an environment is the elimination as far as may be possible of all those external influences which under more normal circumstances would affect the behaviour of the portion of matter considered, but which are of no immediate interest to the observer, and only interfere with his search for the effect of some special influence with which he is at the moment directly concerned, and which is allowed by the special circumstances of the experiment to have full play.

Such a portion of matter so situated may be termed a "system," and although its material constitution may not be simple, yet, by a strict limitation of the number of external influences operating on it and by a restriction of the number of properties observed, it may be possible to regard it as a system of a simple nature. By the removal of artificial limitations and the direction of the attention to a wider circle of properties the system becomes more and more complex. Thus a small quantity of dry air, confined in a glass tube above mercury, whose temperature is maintained constant, is an example of an extremely simple system whose change of volume under change of external pressure is the sole point

of interest for the observer. The system would be equally simple if the pressure were maintained constant and observation directed towards change of volume caused by change of temperature. The system becomes more complex if both pressure and temperature are allowed to vary, but the information already obtained from the simple cases enables us to predict (with success as it so happens in this case) what happens under the wider operation of external influences. If we now consider a portion of matter consisting of air and water, the system, now having two distinct phases (an air-vapour phase and a liquid phase), is more complex, inasmuch as we naturally observe two quantities, viz., the volume of each phase, when conditions of pressure and temperature are varied. Information derivable from the study of such a system and of others still more complex, is applied by the meteorologist to large tracts of our atmosphere or may even be of service in general considerations concerning the atmosphere as a whole regarded as a single but very complex system.

Systems are sometimes defined as "physical" or "chemical" according as the observations made are related to change in physical properties or in chemical constitution, but the terms are not always definite and no clear separation into two classes is in general possible. We shall use the term "physical system" to embrace all systems in which chemical as well as physical properties are observed and to which the epithet "physico-chemical" might be attached save for its clumsiness as a word.

Historically, the systems which were the first to be treated successfully by the methods of exact observation and mathematical analysis initiated in the sixteenth and seventeenth centuries, are the mechanical devices, bodies moving on or near the earth's surface and the system of planets and satellites attendant on the sun. Here the observed properties are the relative positions of the various bodies or parts of the system and the changes produced by the forces acting mutually between the various parts or exerted on them by bodies external to the system. The famous laws of motion propounded by Newton as an adequate summary of the

experimental facts, and applied by him with wonderful skill and success to a wider range of such phenomena, were extended and provided with a very complete mathematical formulation by D'Alembert, Lagrange, Laplace, Hamilton and others. Such formulations became known as various analytical ways of stating the "Principles of Dynamics," and a system of bodies in which the movement of its parts (assumed to conform exactly with these principles) is the prime object of observation is termed a "dynamical system."

However, motion is only one of the observable features of any collection of bodies. Properties such as temperature, pressure, quantity of heat, luminosity, colour, refractivity, magnetic induction, electric charge and potential, chemical constitution, reactivity, etc., claim our attention. For some time several of these properties were explained by postulating the existence of subtle and weightless forms of matter, not accessible to direct observation, such as "caloric," "magnetic and electric fluids." But the influence of the mathematical physics of the eighteenth century, with its treatment of the movement of a finite body as arising from the interaction of the discrete "particles" constituting the body and from their response to external forces, gave an irresistible impulse towards the explanation of all physical and chemical properties of matter as manifestations of the configuration and motion of the ultimate particles of the matter. It was not an accidental circumstance, but one quite natural in the mental environment of the time, that Dalton should have been led to the formulation of his atomic hypothesis by considerations of a mathematical-physical rather than of a purely chemical nature. There followed in quick succession the dynamical theory of heat, the kinetic theory of gases, the molecular theory of magnetism, all meeting with stubborn resistance but all winning recognition by their power in summarising experience and by the ultimate identity of the underlying ideas in each case. Finally, as the pinnacle of this edifice, built on a dynamical view of all properties of matter, there was constructed the theory that radiation is ultimately a propagation of an actual wave motion in a medium possessing elastic and

inertial properties like solid matter, those properties themselves being thrown back in the writings of Cauchy and others on the interaction of ultimate ether particles far surpassing material atoms in minuteness and fineness of structure. Even biological science could not evade the influence of these ideas, and in the nineteenth century there was for a time a great vogue in the idea that in some way life and consciousness are but the by-products of the mechanical reactions between the ultimate atoms of living tissue, whose movements are just as much determined by the laws of dynamics as are those of the planets in our solar system. To be sure such crude notions have had their day in biology, and even in physical science, "atoms interacting across empty space" and "waves pulsating through the luminiferous ether" are strongly suspect. But although the conceptual entities which we employ in order to give our minds an orderly picture of the apparently inextricable complexity of natural phenomena are being replaced at the moment by new and as yet unfamiliar concepts, there still remains as powerful as ever and absolutely indispensable the great body of mathematical analysis which has grown up with the physical science of the past two or three centuries; and in that body analytical dynamics holds a fundamental place for the reasons already stated.

This mechanical conception of the underlying nature of physical phenomena is familiar enough to anyone conversant with the usual texts of Physics and Chemistry. The notions are entirely plausible in a qualitative or roughly quantitative sense. It is when one goes into the matter in some detail and attempts to apply mathematical methods in order to produce quantitatively precise or nearly precise results that trouble begins. Molecular systems are much too complex to follow in detail with the aid of dynamical laws and hypotheses as to the nature of intermolecular forces or intramolecular and intermolecular electromagnetic fields. To make any headway at all the laws of probability have to be impressed into service and made to co-operate with dynamical principles. The worker is involved at once in statistical considerations, and this combination of statistical calcula-

tions with dynamical reasoning is called "Statistical Mechanics." Fortunately, for those not too conversant with dynamical methods, considerable progress in this subject can be made towards tangible results without any greater knowledge of mechanics than that possessed by the average student at the end of a University second year in the Applied Mathematics class room. At a pinch one can manage along for a time on even less. In this book every effort is made to keep at first to illustrations of such a nature that a detailed knowledge of dynamical methods, such as those employing the Lagrange and Hamilton equations of motion, is not required. For a satisfactory foundation, however, of the postulates upon which we base the statistical calculations, a knowledge of Hamilton's equations is required. Still, we shall assume that the postulates, explained at the outset, are all right, and make use of them at once, deferring their justification to the last chapters of the book. This appeals to the author as being probably the manner of laying out the work, which will evoke the interest of the reader at once. As regards pure statistics, little more is needed than an elementary knowledge of permutations, such as is available in any algebra text, and of the binomial and multinomial theorems. It is assumed, of course, that the reader has some knowledge of the symbolism and methods of the calculus. Any special mathematical information beyond this is supplied in appendices.

CHAPTER I

STATISTICAL METHOD

1.1 The Spin of a Coin.—It is a commonplace statement that on spinning a penny the chances are equal that it will present a head or tail. The *à priori* probability of either is 0.5. The use of the epithet "*à priori*" might lead us to infer that this is a statement deduced from our "inner consciousness" or some equally mysterious source. Not so; it is a bald statement of the *experimental* fact that if anyone chooses to amuse himself for some time by tossing a coin repeatedly and at random, he will find the ratio of heads to tails always close to unity, and the more so the longer he proceeds with the entertainment. There are two aspects presented by the fallen coin, and one has as good a chance of showing itself as the other.

Suppose we spin two coins. How many "complexions" are possible? There are four, since the two pennies may both present heads or both tails, or the first penny may present a head and the second a tail, or *vice versa*. Any one of these is as probable as any other, since the events are independent; for the fall of one coin (say) head up, does not bias the fate of the other. Thus the *à priori* probability of each of the four complexions is 0.25, and any "doubting Thomas" can overcome his scepticism by trying it. He will find that on making a large number of throws practically one quarter of them will yield any given complexion.

There are four complexions, but three "statistical states":—(1) both pennies showing heads, (2) both showing tails, (3) one showing a head and one a tail. Two complexions fall within state (3), and so the probability of that state is 0.5, while that of the states (1) and (2) are 0.25 each. State (3) is twice as probable as either (1) or (2).

Increase the number of coins thrown to three. There are eight complexions. Here they are :—

| | First Penny. | | Second Penny. | | Third Penny. |
|-----|--------------|-----|---------------|-----|--------------|
| (1) | ... Head | ... | Head | ... | Head |
| (2) | ... Head | ... | Head | ... | Tail |
| (3) | ... Head | ... | Tail | ... | Head |
| (4) | ... Head | ... | Tail | ... | Tail |
| (5) | ... Tail | ... | Head | ... | Head |
| (6) | ... Tail | ... | Head | ... | Tail |
| (7) | ... Tail | ... | Tail | ... | Head |
| (8) | ... Tail | ... | Tail | ... | Tail |

All are equally probable, having $\frac{1}{8}$ as their *a priori* probability. There are four statistical states, viz. :—

- (1) All heads.
- (2) All tails.
- (3) Two heads and one tail.
- (4) One head and two tails.

Only one complexion falls within either state (1) or (2), but three within either of the third and fourth states. Hence the states (3) and (4) are each thrice as probable as (1) or (2). The probabilities are $\frac{1}{8}$, $\frac{1}{8}$, $\frac{3}{8}$, $\frac{3}{8}$.

It should require little thought now to extend the reasoning to any number of coins. Let there be n coins, and suppose we indicate the fact that the r^{th} coin presents a head by the symbol a_r , and that it presents a tail by the symbol b_r . Then any complexion presented by a fall of the n coins will be represented by some such expression as—

$$a_1 a_2 b_3 a_4 b_5 \dots a_n.$$

Each term will consist of n symbols. In every term, the suffixes will proceed regularly from 1 to n , but the arrangement of the a and b symbols will be fortuitous. Thus the term written represents a complexion in which the first penny falls head up, the second head up, the third tail up, the fourth head up, the fifth tail up, etc., the last head up. We can find all the possible complexions by working out the product of the n factors

$$(a_1 + b_1) (a_2 + b_2) (a_3 + b_3) \dots (a_n + b_n) . (1.1.1)$$

There are 2^n terms ; in each of them any suffix can only

occur once as no penny can show both a head and a tail in one fall. The *à priori* probability of each complexion is therefore 2^{-n} . How many statistical states are there and what is the probability of each? A state, *e.g.*, in which r pennies show heads and s show tails ($r + s = n$) will include all those complexions whose symbolic terms contain r of the a symbols and s of the b symbols. If we wish to find the number of these complexions we obliterate the suffixes in (1.1.1) and consider the coefficient of $a^r b^s$ in the product $(a + b)^n$. By the binomial theorem this is

$$\frac{n!}{r! s!}$$

Each of the complexions has an *à priori* probability 2^{-n} . Hence the probability of the statistical state mentioned is

$$\frac{n!}{r! s!} \left(\frac{1}{2}\right)^n \quad (1.1.2)$$

There are, of course, as many statistical states as there are terms in the expansion of $(a + b)^n$, *i.e.*, $n + 1$.

The reader should bear in mind the experimental basis of these calculations. The results might have been otherwise. If by some edict of the Master of the Mint pennies were so loaded that each one fell twice as often head up as tail up, the *à priori* probability of a head would be $2/3$, of a tail, $1/3$. To take account of the increased chance of a head being shown by any coin we must in the reckoning of complexions consider the product

$$(2a_1 + b_1) (2a_2 + b_2) \dots (2a_n + b_n).$$

The coefficient of any term will give the number of times which the corresponding complexion will turn up on the average out of 3^n tosses. Thus a complexion in which r *particular* pennies turn up heads and the remaining s tails will have an *à priori* probability of $(2/3)^r (1/3)^s$ or $2^r/3^n$. So the probability of the statistical state, r heads and s tails would no longer be the coefficient of $a^r b^s$ in

$$\left(\frac{1}{2}a + \frac{1}{2}b\right)^n$$

but in

$$\left(\frac{2}{3}a + \frac{1}{3}b\right)^n$$

In general, if the *à priori* probabilities of a head and a tail were respectively p and q ($p + q = 1$), the probability of the statistical state mentioned would be the coefficient of $a^r b^s$ in

$$(pa + qb)^n,$$

i.e.,

$$\frac{n!}{r! s!} p^r q^s \quad . \quad . \quad . \quad (1.1.3)$$

1.2 Throwing of Dice.—If we were to use dice instead of coins, we should have six possibilities with each die, not merely two as in the case of coins. Each aspect of a die has an *à priori* probability $1/6$, if the dice are not loaded. Let a throw of one by the r^{th} die be symbolised by a_{1r} , of two by a_{2r} , etc., of six by a_{6r} . We can symbolise a given complexion in which, say, the first die throws a three, the second die a five, the third a five, the fourth a one, the fifth a two, the sixth a four, the seventh a three, etc.—the n^{th} a two by the expression

$$a_{31} a_{52} a_{53} a_{14} a_{25} a_{46} a_{37} \quad . \quad . \quad . \quad . \quad a_{2n}$$

In any such symbolic term the second suffix advances regularly from 1 to n , but the first is fortuitously chosen from 1 to 6. Any possible complexion is represented by some one of the 6^n terms obtained by expanding the product of the n factors.

$$(a_{11} + a_{21} + \dots + a_{61}) (a_{12} + a_{22} + \dots + a_{62}) \\ \dots \dots \dots (a_{1n} + a_{2n} + \dots + a_{6n}) \quad (1.2.1)$$

Each complexion has an *à priori* probability of 6^{-n} .

We can find the number of different complexions within the statistical state, in which n_1 dice throw a one, n_2 dice throw a two, etc., n_6 dice throw a six, by eradicating the second suffix in (1.2.1) and calculating the coefficient of the term.

$$a_1^{n_1} a_2^{n_2} a_3^{n_3} a_4^{n_4} a_5^{n_5} a_6^{n_6}$$

in the expansion of

$$(a_1 + a_2 + a_3 + a_4 + a_5 + a_6)^n$$

In any text-book of algebra the reader will find in the chapter on the multinomial theorem that this is

$$\frac{n!}{n_1! n_2! n_3! n_4! n_5! n_6!}$$

Thus the probability of this statistical state is

$$\frac{n!}{n_1! n_2! n_3! n_4! n_5! n_6!} \left(\frac{1}{6}\right)^n \quad (1.2.2)$$

If the dice had been loaded alike, so that the *a priori* probability of a throw of a one by any die were p_1 , of a two, p_2 , etc., ($p_1 + p_2 + p_3 + p_4 + p_5 + p_6 = 1$), the probability of the state mentioned would be the coefficient of $a_1^{n_1} a_2^{n_2} a_3^{n_3} a_4^{n_4} a_5^{n_5} a_6^{n_6}$ in

$$(p_1 a_1 + p_2 a_2 + p_3 a_3 + p_4 a_4 + p_5 a_5 + p_6 a_6)^n,$$

i.e.,

$$\frac{n!}{n_1! n_2! n_3! n_4! n_5! n_6!} \cdot p_1^{n_1} p_2^{n_2} p_3^{n_3} p_4^{n_4} p_5^{n_5} p_6^{n_6} \quad (1.2.3)$$

The extension of these results is now an easy matter. Let there be n similar articles each one of which can present at one time one of c different aspects, the *a priori* probability of each aspect being $p_1, p_2, p_3, \dots, p_c$ respectively, then the probability of the statistical state in which n_1 articles present the first aspect, n_2 the second aspect, etc., n_c the c^{th} aspect is

$$\frac{n!}{n_1! n_2! \dots n_c!} p_1^{n_1} p_2^{n_2} \dots p_c^{n_c} \quad (1.2.4)$$

the first factor being the number of complexions consistent with these aspects.

The total number of possible complexions, being the number of separate terms in a product of n factors each containing c terms, viz.,

$$(a_{11} + a_{21} + \dots + a_{c1})(a_{12} + a_{22} + \dots + a_{c2}) \dots (a_{1n} + a_{2n} + \dots + a_{cn})$$

is, of course, c^n . On the other hand, the number of statistical states is the number of terms in the expansion

$$(a_1 + a_2 + \dots + a_c)^n$$

which is, therefore, the number of "homogeneous products" of the c quantities a_1, a_2, \dots, a_c , each product being of the n^{th} degree. Reference to a text-book of Algebra will show that this is

$$\frac{(n + c - 1)!}{n! (c - 1)!} \quad . \quad . \quad . \quad (1.2.5)$$

1.3 The Normal Law of Errors.—We shall now consider a modification of this random throwing of a number of articles which will lead to the introduction of a mathematical function which at a later stage plays an important part in statistical-mechanical reasoning.

Instead of coins or dice, let us have in our possession n counters, each one being labelled $+\epsilon$ on one side and $-\epsilon$ on the other. On throwing these, any complexion will, if we add the numbers showing, yield a sum $m\epsilon$ where m is a positive or negative integer lying between $-n$ and $+n$. In fact m is $r - s$ where r counters show positive faces and s counters show negative; thus the probability of the sum $m\epsilon$ is given by the number of complexions corresponding to (r, s) . It is

$$\frac{n!}{r! s!} \left(\frac{1}{2}\right)^n \quad . \quad . \quad . \quad (1.3.1)$$

where

$$\begin{aligned} r + s &= n \\ r - s &= m \end{aligned}$$

By a well known result, the expression (1.3.1) is maximum when $r = s$, and the value decreases progressively to the amount $(\frac{1}{2})^n$ as the difference $r - s$ or $s - r$ increases in numerical value from zero to n . Thus the state in which the sum is zero is the most probable, and if n is a very large number, the probability of those states in which the sum is zero or only a small multiple of ϵ , far outweighs the probability of those in which the sum takes a relatively large numerical value. It will be both interesting and serviceable

to investigate the limiting form for this expression (1.3.1) when ϵ is made very small in value and the number n grows without limit. This condition is, however, rather vague, for it makes no provision for the maximum value of the sum, viz., $n\epsilon$. We can make the condition sufficiently precise by postulating that $n\epsilon$ may also increase without limit as ϵ decreases and n increases, but in such a manner that the product of the maximum value of the sum, $n\epsilon$, and the common difference, 2ϵ , between consecutive values of the sum remains finite and constant. Thus write

$$2n\epsilon^2 = k^2$$

where k is a finite constant. So as not to interrupt the general course of the reasoning we relegate some rather tedious mathematical steps to an appendix where it is shown that in the limit the expression (1.3.1) is equal to

$$\frac{1}{k\pi^{\frac{1}{2}}} \exp\left(-\frac{z^2}{k^2}\right) \delta z \quad . \quad . \quad . \quad (1.3.2)^*$$

where z is written for $(r-s)\epsilon$ and $\delta z = 2\epsilon$.

Thus it appears that the probability that the sum lies between the values ζ_1 and ζ_2 , is given by the expression

$$\frac{1}{k\pi^{\frac{1}{2}}} \int_{\zeta_1}^{\zeta_2} \exp\left(-\frac{z^2}{k^2}\right) dz \quad . \quad . \quad . \quad (1.3.3)$$

It is a well known result that the value of the integral in (1.3.3) between the limits $-\infty$ and $+\infty$ is $k\pi^{\frac{1}{2}}$, and so the expression (1.3.3) when ζ_1 is $-\infty$ and ζ_2 is $+\infty$ is unity, as, of course, it must be since the sum of the probabilities of all possible states must be unity.

The integral

$$\int e^{-az^2} dz$$

plays an important part in statistical-mechanical analysis, as we shall see later, and a number of its most useful properties are summarised in the appendix. But before passing

* The series

$$1 + \frac{y}{1!} + \frac{y^2}{2!} + \frac{y^3}{3!} + \dots + \frac{y^n}{n!} + \dots \text{ad. inf.}$$

is written $\exp(y)$. It is, of course, equal to e^y , if y is a real quantity.

on to the application of the results of this chapter to molecular systems, it may be as well to point out that we have in this section been treating an important case in the Theory of Errors of Observations.

We may assume that the accidental error in an observation made with a definite instrument is the algebraic sum of a number of component errors of the instrument due to change in external conditions, uncorrected errors of the instrument and peculiarities of the observer. Each of these components may in its turn be regarded as due to a large number of elementary causes, so that we are not violating any obvious truth in assuming that an accidental error of observation is the algebraic sum of a very great number of very small errors. Suppose we make a further simplifying assumption (which can only be justified by subsequent comparison of the results of making it with the facts) that all these elementary errors have the same *numerical* magnitude, but are as likely to be positive as negative. Thus if there are n elementary errors altogether, each of magnitude ϵ , the actual error will in any observation have the magnitude $(r - s)\epsilon$ if r of the elementary errors are positive and s are negative in that observation. But such an outcome will have the same probability as in the case of the counters, where r came down positive and s negative. That is, the probability of the error $(r - s)\epsilon$ is given, by (1.3.1), and proceeding as before we find that if the true value of the quantity observed is a , the chance that an observation gives a value lying between $a + \zeta_1$ and $a + \zeta_2$ is indicated by the expression (1.3.3). But those interested may refer to the appendix for further information. It is more to our purpose to proceed to the study of molecular systems, and the reader can glance at the appendix when at a later stage he is compelled to know something about the integral.

$$\int e^{-az^2} dz.$$

APPENDIX TO CHAPTER I

ON THE NORMAL LAWS OF ERRORS

THE problem raised in section (1.3) is to obtain a function of a *continuous* variable z which shall replace

$$\frac{n!}{r!s!} \left(\frac{1}{2}\right)^n$$

this being a function of a quantity $(r - s)\epsilon$ which varies by discrete amounts 2ϵ . Implicitly we have somewhat changed our point of view. Previously an error which was not an *integral* multiple of ϵ , was not supposed to occur at all; its probability was zero; probabilities were, so to speak, concentrated on definite errors. Now all errors are possible from $z = -\infty$ to $z = +\infty$, and, what may appear paradoxical at first sight, the probability that the error may have any definite value is zero. But this is only natural as the number of possible errors now is unlimited, and the chance for any one of them is one in infinity, or nothing at all. The form of the statement must now be that there exists a function of z , $f(z)$, such that the probability that the error shall lie between the values $z = \zeta_1$ and $z = \zeta_2$ will be given by the integral

$$\int_{\zeta_1}^{\zeta_2} f(z) dz,$$

and to find $f(z)$ we must proceed on the assumption that there is an approximate equality between

$$f(z) \delta z$$

and

$$\frac{n!}{r!s!} \left(\frac{1}{2}\right)^n$$

where $z = (r - s)\epsilon$ and $\delta z = 2\epsilon$, the approximation being closer and closer the smaller ϵ , and therefore the larger r and s (and, of course, n) for a given value of z . The reader is warned against a too common misconception that $f(z)$ is the chance of an error z . He is asked to bear in mind that

the function which replaces $(n! / r! s!) \cdot 2^{-n}$ is not $f(z)$, but $f(z) \delta z$. The infinitesimal is as important a factor of the function as $f(z)$ itself. The probability which was previously concentrated on a distinct value of z is now as it were spread over a small neighbouring range of values.

Writing m for $r - s$, we have

$$2 \epsilon f(m \epsilon) \doteq \frac{n!}{r! s!} \left(\frac{1}{2}\right)^n$$

and also

$$2 \epsilon f(m \epsilon + 2 \epsilon) \doteq \frac{n!}{r + 1! s - 1!} \left(\frac{1}{2}\right)^n$$

Hence

$$\frac{f(m \epsilon + 2 \epsilon)}{f(m \epsilon)} \doteq \frac{s}{r + 1}$$

and so

$$\frac{f(m \epsilon + 2 \epsilon) - f(m \epsilon)}{f(m \epsilon + 2 \epsilon) + f(m \epsilon)} \doteq - \frac{r - s + 1}{r + s + 1} \doteq - \frac{m + 1}{n + 1},$$

or

$$\frac{f(m \epsilon + 2 \epsilon) - f(m \epsilon)}{2 \epsilon} \doteq - \frac{m + 1}{2(n + 1)} \left[f(m \epsilon + 2 \epsilon) + f(m \epsilon) \right]$$

On writing z for $m \epsilon$, δz for 2ϵ and k^2 for $2n \epsilon^2$, and proceeding to the limit, we obtain

$$\frac{d f(z)}{d z} = - \frac{2 z}{k^2} f(z).$$

This is equivalent to

$$\frac{d \log f(z)}{d z} = - \frac{2 z}{k^2}.$$

Hence

$$\log f(z) = - \frac{z^2}{k^2} + \text{constant},$$

or

$$f(z) = A \exp \left(- \frac{z^2}{k^2} \right).$$

The integration constant A is to be determined by the fact that

$$\int_{-\infty}^{\infty} f(z) d z = 1,$$

since the integral represents the sum of all the probabilities and must be unity.

Before proceeding it may be as well to state briefly a number of results concerning the integral

$$\int e^{-az^2} dz$$

and kindred integrals. These will prove serviceable in later chapters. By a simple change of variables, $x = za^{\frac{1}{2}}$, we can write for this integral

$$a^{-\frac{1}{2}} \int e^{-x^2} dx.$$

First of all it can be shown that if the integral is taken between the limits $x = -\infty$ and $x = +\infty$, we obtain

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \pi^{\frac{1}{2}}$$

Since e^{-x^2} is an even function of x , it is also true

$$\int_0^{\infty} e^{-x^2} dx = \frac{1}{2} \pi^{\frac{1}{2}}.$$

The value of

$$\frac{2}{\pi^{\frac{1}{2}}} \int_0^{\infty} e^{-x^2} dx$$

is a function of η , which increases from zero to unity as η increases from zero to infinity. Tables of this function for definite values of η are printed in text-books on the Theory of Errors.* If η is equal to 0.1 the expression is about 0.1125; if η is equal to 0.5, it is 0.5205; for η equal to 1, the value is 0.8427; and by the time η has reached 3, the expression has attained the value 0.99998; so that the integration from 3 to ∞ contributes only 0.00002 of the value to the function of η . One can realise the truth of this in a general way by noting that if $x = 0.1$, $e^{-x^2} =$

* See for example, *Combinations of Observations*, Brunt. A table is also printed in Jeans' *Dynamical Theory of Gases*.

0.99905, while if $x = 3$, $e^{-x^2} = .00012$, and beyond this e^{-x^2} decreases to very minute values with great rapidity.

It can also be shown that

$$\int_0^{\infty} x^n e^{-x^2} dx = \frac{1}{2} \cdot \left(\frac{n-1}{2} \right)!$$

if the index n is an odd integer, and

$$\int_0^{\infty} x^n e^{-x^2} dx = \frac{n!}{2^{n+1} \cdot \frac{n}{2}!} \pi^{\frac{1}{2}},$$

if n is an even integer.

The cases of this which we shall require now and at a later stage are

$$\int_0^{\infty} x e^{-x^2} dx = \frac{1}{2}$$

$$\int_0^{\infty} x^2 e^{-x^2} dx = \frac{\pi^{\frac{1}{2}}}{4}$$

$$\int_0^{\infty} x^3 e^{-x^2} dx = \frac{1}{2}$$

$$\int_0^{\infty} x^4 e^{-x^2} dx = \frac{3 \pi^{\frac{1}{2}}}{8}$$

We can now determine the constant A in the equality above

$$\begin{aligned} f(z) &= A \exp \left(-\frac{z^2}{k^2} \right) \\ &= A e^{-az^2}, \end{aligned}$$

where we write a for $1/k^2$. For if

$$A \int_{-\infty}^{\infty} e^{-az^2} dz = 1,$$

then

$$A = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}}$$

since

$$\int_{-\infty}^{\infty} e^{-\alpha z^2} dz = \frac{1}{\alpha^{\frac{1}{2}}} \int_{-\infty}^{\infty} e^{-x^2} dx = \left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}}$$

Thus the chance that an error may fall between the values $z = \zeta_1$ and $z = \zeta_2$ is

$$\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{\zeta_1}^{\zeta_2} e^{-\alpha z^2} dz.$$

This law has been deduced with the aid of rather restrictive assumptions concerning the nature of the causes giving rise to errors. Actually, rather broader assumptions can form a starting point for its deductions, and it is found to be closely followed in many cases. Of course in some circumstances other error laws hold; e.g., if the restriction that positive elementary errors are as likely as negative be removed, we cannot arrive at a function symmetrical in value with respect to the origin.

The reader will naturally inquire as to the part played by the constant k (or α) in the law. The way in which it was introduced (as equal to $\epsilon(2n)^{\frac{1}{2}}$), gives no clear indication of this; but we can easily arrive at a conclusion concerning it by inquiring into the average error made in a large series of observations which conform to the normal law. The equal preponderance of positive and negative elementary errors shows that the average of the observations is the true value of the quantity observed, denoted by a . The chance that an observation lies between $a + z$ and $a + z + \delta z$ is $(\alpha/\pi)^{\frac{1}{2}} e^{-\alpha z^2} \delta z$. Now as negative and positive values of the error z are equally likely, the average error in the strict algebraic sense is zero; but this is of no help to us. However, we can find the average *numerical* value of the errors if we multiply the *numerical value* of z by its probability $(\alpha/\pi)^{\frac{1}{2}} e^{-\alpha z^2} \delta z$, and sum over the whole range, i.e., integrate from 0 to ∞ .

So

$$\begin{aligned}\bar{z} &= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} 2 \int_0^{\infty} z e^{-\alpha z^2} dz \\ &= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \frac{2}{\alpha} \int_0^{\infty} x e^{-x^2} dx \\ &= \frac{1}{(\pi \alpha)^{\frac{1}{2}}} \\ &= \frac{k}{\pi^{\frac{1}{2}}}\end{aligned}$$

Another important manner of estimating an average value for the error is to square each error, multiply this by the probability in each case, and sum over all the errors. This result gives us the mean square of the errors, and the square root of it is called the "mean square error" (M.S.E.). Thus we find

$$\begin{aligned}\bar{z}^2 &= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} z^2 e^{-\alpha z^2} dz \\ &= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \frac{1}{\alpha^{\frac{3}{2}}} \int_{-\infty}^{\infty} x^2 e^{-x^2} dx \\ &= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \frac{1}{\alpha^{\frac{3}{2}}} \frac{\pi^{\frac{1}{2}}}{2} \\ &= \frac{1}{2\alpha} \\ &= \frac{k^2}{2}\end{aligned}$$

and so the M.S.E. is $k/2^{\frac{1}{2}}$, and the ratio of the average numerical error to the M.S.E. is $(2/\pi)^{\frac{1}{2}}$ or 0.798.

Still another result concerns what is called the "median error," which has such a value that if we denote it by r , then half the errors lie between $-r$ and $+r$. This quantity is determined by the equality

$$\left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} \int_0^r e^{-\alpha z^2} dz = 0.5$$

or
$$\left(\frac{1}{\pi}\right)^{\frac{1}{2}} \int_0^{ra^{\frac{1}{2}}} e^{-x^2} dx = 0.5.$$

From the tables of $\int_0^{\eta} e^{-x^2} dx$, it can be found that $ra^{\frac{1}{2}}$ has the value 0.4770, or $r = .4770 k$.

It is clear then that the value of the constant k indicates the standard of precision of the measurements made. The smaller k is the more accurate has been the series of observations. Of course all this implies that care and skill have already been expended on the actual observational work. No amount of tinkering with the theory of errors is going to draw reliable conclusions from careless measurements.

CHAPTER II

THE STATISTICS OF A SIMPLE MOLECULAR SYSTEM

2.1 The Complexions of a Molecular System. Configurations.—We begin our statistical-mechanical investigations by applying the methods developed in the previous chapter to a simple body which is conceived to be an aggregate of molecules, each molecule being regarded as having no structure, but merely possessing minute mass and extension—in short the “particle” of dynamical theory. Any obvious changes in the body must, of course, be associated with unobservable but yet actual changes in the relative configuration and motions of the particles; but, to be sure, a great deal of change might be going on in the relative situations and movements of the molecules without any observable difference manifesting itself in the general appearance and behaviour of the body.

The configuration of the molecular system can only be precisely defined by assigning definite co-ordinates to each particle (the particles for the moment being regarded as equivalent to points), and as the configurations possible for a given volume of the body are therefore unlimited in number it is impossible to deal with statistical states by counting the number of configurations consistent with each state, since these are uncountable. In the Theory of Errors we regard an error as having a calculable chance if it lies in an assigned range of errors; so in the example before us we regard a complexion of the molecules as defined by assigning a range of configuration. In short, we do not say that a particular molecule is at a definite point (x, y, z) , but that its co-ordinates lie between x and $x + \delta x$, y and $y + \delta y$, z and $z + \delta z$ where δx , δy , δz are assigned small quantities. In other words, we divide the volume occupied by the body into a *finite* number of “cells,” and state that such and such

molecules are at the moment situated in such and such cells. As far as the counting of complexions is concerned, we regard the molecules as analogous to the coins or dice of the previous chapter. The existence of a molecule in an assigned cell is analogous to the exhibition of a certain aspect by a coin or die. So long as a molecule remains in the same cell, its "aspect" is unchanged. A "complexion" of the system is defined by the particular aspects shown by the individual molecules, *i.e.*, by the way the individual molecules are distributed among the cells. Merely to move the molecules about within the cells does not alter the complexion; but the transfer of molecules from cell to cell will alter the complexion even although it is only an interchange which leaves the number (but not the individuality) of the molecules in the cells unaltered. The smaller the cells and the greater their number, the finer is the detail, so to speak, which distinguishes one complexion from another, but in order to render counting conceivably possible, the size of each cell must remain finite and the number of them also finite, though possibly very large. We shall see later that in carrying on the mathematical analysis after the counting has been effected, we may have to resort to integrations which imply infinitesimal elements of volume unlimited in number in much the same way as in Chapter I. we passed from summation over a range of discrete numbers to integration throughout a range of a continuous variable; but in the initial stages of the analysis the assumption of finite cells is necessary for beginning the calculation at all.

If, therefore, there are n molecules and c cells, we find just as in section (1.2) that the number of complexions in which n_1 molecules are in the first cell, n_2 in the second cell, etc.,, n_c in the c^{th} cell is

$$\frac{n!}{n_1! n_2! \dots n_c!} \quad . \quad . \quad . \quad (2.1.1)$$

We shall in future denote this number by the functional symbol

$$W(n_1, n_2, \dots, n_c).$$

All this is, of course, a mere matter of counting. Many of

these complexions would entail the crowding of the body into one small portion of the volume within its external surface. Indeed there are c complexions in which all the molecules would be in one cell. But this consideration need not deter us from proceeding; for if we make the proviso that the cells though small enough to make c a large number, are yet large enough to contain a large number of molecules at the average density, so that in fact the ratio of n to c is also large, then it is possible to show that in all but a *relatively* small number of complexions the molecular density is uniform or sufficiently near uniformity for the discrepancy to be undetectable by experimental means. It is, of course, easy to see that $W(n_1, n_2, \dots, n_c)$ is increased in value if in the denominator two numbers, n_r and n_s , in any pair of factorials are replaced by two other integers which have the same sum, but are more nearly equal to one another.

For

$$\begin{aligned} & (k+l)! (k-l)! \\ &= (k+l) (k+l-1) \dots (k+1) \cdot k! \times \\ & \quad \frac{k!}{(k-l+1) (k-l+2) \dots (k-1) k} \\ &> k! k! \end{aligned}$$

and therefore

$$\frac{1}{(k+l)! (k-l)!} < \frac{1}{k! k!}$$

Thus the state in which the density is uniform embraces a number of complexions which is greater than for any other state in which the numbers n_1, n_2, \dots, n_c are given, but are not all equal to n/c .* But to prove the statement concerning the preponderance in number of the complexions corresponding to uniform density or states near it over all other complexions requires closer analysis than this; and to proceed with the proof we require the assistance of an approximation to $W(n_1, n_2, \dots, n_c)$, which, however,

* We suppose the number of molecules and number of cells to be so chosen that n/c is an integer.

has to be used with due consideration for the conditions under which it is true.

There is a famous theorem published early in the eighteenth century by the Scottish mathematician James Stirling, which states that there is an approximate equality between the logarithm (to the Napierian base) of the factorial of n and the expression

$$\left(n + \frac{1}{2}\right) \log_e n - n + \frac{1}{2} \log_e 2\pi.$$

Provided n is as large as 10, for example, a four-figure logarithm table will not reveal the discrepancy, and for sufficiently large numbers, it is possible to write

$$\log n! = n \log n - n.$$

(See the appendix for some remarks on Stirling's theorem.)

From this it follows that, provided none of the numbers n_r are too small,

$$\log W(n_1, n_2, \dots, n_c) \doteq n \log n - \sum_{r=1}^c n_r \log n_r \quad (2.1.2)$$

With the aid of this approximation one can prove the assertion made above. The details of the proof will be found in the appendix to this chapter, and the outcome is to demonstrate as we have already said, that the statistical states in which the molecules are uniformly distributed, or distributed in such a manner that the number in each cell differs but little from the average, embrace all but a negligible fraction of the total complexions. The point of this important result will appear presently.

2.2 The Complexions of a Molecular System. Phases.—

In the previous section we confined our attention to the arrangements of the molecules in space; but, of course, in any attempt to explain the general properties of matter by dynamical theory, we must also take account of the motions of the molecules relative to the frame of reference in which the body as a whole is regarded as fixed. Since the molecules are regarded as particles, it is easy to conceive a graphical representation of a precise velocity-condition. Choosing an origin, the velocity of a particle can be represented by the

position of a point in a "velocity-diagram," the vector from the origin to the point representing the magnitude and direction of the velocity. Thus the actual velocities of the n particles at any time are represented by a configuration in the velocity-diagram of the n representative points. This diagram can, of course, be divided into cells as in the case of the volume occupied by the body; velocity-complexions can be defined just as before and the number of complexions embraced in any velocity-state (where velocities within narrow limits are assigned without reference to the individuality of the molecules) can be counted and comparisons of relative numerical strength be made.

It is customary to link up the two methods of partitioning into one "picture." The configuration and velocity of each molecule is regarded as an entity with six components, three position-components and three velocity-components, and is called a "phase" of the molecule. When precise values of velocity and position are assigned to each molecule in the system, we are said to have prescribed a "phase of the system." As before, the phases possible to the system are unlimited in number, and no progress can be made in counting complexions unless a complexion is regarded not as a phase, but an arrangement of the molecules in a small but finite "extension-in-phase." That is, we do not designate an "aspect" of a molecule by saying that its position and velocity are given by components x, y, z, u, v, w , but by saying that the first co-ordinate lies between x and $x + \delta x$, etc.; the first velocity-component between u and $u + \delta u$ etc., where $\delta x, \dots, \delta w$ are finite but small increments. We can visualise as small rectangular figures the forms to which we attach the symbols, and regard $\delta x \delta y \delta z$ and $\delta u \delta v \delta w$ as their volumes. With no possibility of visualising, we nevertheless refer to the magnitude $\delta x \delta y \delta z \delta u \delta v \delta w$ as an element of "extension-in-phase," and for convenience and brevity call it a "phase-cell," borrowing the geometric term from our earlier considerations. Indeed, in a great deal of the literature of the subject, geometrical language is used in a manner which at the outset may dismay the beginner, who imagines he is called upon to perform the

feat of "seeing" a space of six or more dimensions. He may reassure himself; no such impossible task is expected from him. The geometric terms are merely borrowed and attached to analogous ideas; indeed their use can be avoided altogether (*e.g.*, that is the practice of Gibbs), but for the sake of reading the general literature later, the beginner should familiarise himself with this use of geometric terms. For instance, a phase of a molecule which is indicated by assigning definite values to the x, y, z, u, v, w , of the molecule, is referred to as a "point in the six-dimensional phase-diagram." An extension in phase, which is a range of values of position and velocity co-ordinates such that no phase in the range has co-ordinate values outside the six ranges x to $x + \delta x, \dots, w$ to $w + \delta w$, is called a cell of the phase-diagram. We can conceivably visualise the path of a molecule in physical space. It is the geometric counterpart of a continuous series of values of the position co-ordinates. We can also visualise a curve in a velocity-diagram which would represent geometrically the changing values of u, v, w , for a molecule. Indeed the reader has perhaps met it in his academic text-books of mechanics under the name "hodo-graph." When we place the two pictures together, we cannot get a "picture," but we still use the geometric language; the series of continuous phases through which the position and motion of a molecule pass with lapse of time, is called the "phase-path" or "trajectory" of the molecule.

If the reader still experiences any difficulty in this matter of geometric terminology, he may find the following device of some assistance, until he becomes sufficiently familiar to dispense with it. Let him think of three *plane* diagrams, each one provided with the usual pair of rectangular axes. In one let x and u be represented by a point; in the second let y and v be so represented; and in the third, z and w . A phase of a molecule can then be visualised by thinking of three points—one in each diagram; an extension in phase by thinking of three small rectangles; the changing phases of a molecule by thinking of three curves. A "point-group" represents a phase; a "curve-group" represents the history

of the molecule and a "rectangle-group" represents an extension-in-phase. The division of the phase-diagram into cells may be associated in the mind's eye with the cross-meshing of the plane diagrams by lines parallel to the axes. One has to be careful, however. If even one member of a point-group is changed, the phase is altered; we have changed to a different point in the phase-diagram. Keeping two rectangles in the group alike, but changing the third, produces a different phase-cell. Suppose, for example, we have divided a limited portion of the (x, u) diagram into l rectangles, another limited portion of the (y, v) diagram into m rectangles, and of the (z, w) into n rectangles, we are dealing with a limited extension in the phase-diagram which has been divided into $l m n$ cells; for any rectangle in the (x, u) diagram can be combined with any in the (y, v) , and this again with any in the (z, w) , each combination producing a distinct phase-cell.

The algebraic work from this point is just as before. If there are c phase-cells and n molecules, the number of complexions embraced in that state in which the phases of n_1 molecules are within the first cell, etc., of n_c molecules within the c^{th} cell is $W(n_1, n_2, \dots, n_c)$

where

$$W(n_1, n_2, \dots, n_c) = \frac{n!}{n_1! n_2! \dots n_c!}$$

and approximately

$$\log W(n_1, n_2, \dots, n_c) = n \log n - \sum_{r=1}^c n_r' \log n_r.$$

So far there has been no reference to dynamical considerations. We have been concentrating our attention on the concepts necessary for the statistical side of the work. We must now turn our attention to the second member of the double barrelled epithet, "statistical-mechanical."

APPENDIX TO CHAPTER II

A. *Stirling's Theorem*.—A rigorous proof of this theorem, which states that

$$n! = \left(\frac{n}{e}\right)^n (2\pi n)^{\frac{1}{2}} \left(1 + \frac{1}{12n} + \dots\right)$$

can only be appreciated by those who have given some pains to the study of series and their convergency properties. Such a proof will be found by those interested in Chrystal's *Algebra*, Vol. II. Chap. XXX. For a more general theorem which takes the place of Stirling's when n is not an integer, a reference can be made to Whittaker and Watson's *Modern Analysis*, Chap. XII.

For the majority of his readers, the author suspects that a simple empirical test will be quite satisfactory. If any one cares to take the trouble to look up *Napierian* logarithms in a book of tables (the cheap little book prepared by C. G. Knott will suffice), he will find that for instance

$$\log 5 - \frac{\log 1 + \log 2 + \dots + \log 5}{5}$$

has the value 0.6519. He will also find that

$$1 - \frac{\log 10 + \log \pi}{10}$$

has the value 0.6553. If he chooses a larger number 10, he will find that

$$\log 10 - \frac{\log 1 + \log 2 + \dots + \log 10}{10}$$

has the value 0.7922; and that

$$1 - \frac{\log 20 + \log \pi}{20}$$

is also 0.7922, so that a four-figure table cannot distinguish between the values of the two expressions. This empirical procedure gives considerable support to the general result that

$$\log n - \frac{\log 1 + \log 2 + \dots + \log n}{n}$$

$$\doteq 1 - \frac{\log 2 n + \log \pi}{2 n}$$

or

$$\log n! \doteq n \log n - n + \frac{1}{2} \log (2 \pi n).$$

It follows that

$$n! \doteq \left(\frac{n}{e}\right)^n (2 \pi n)^{\frac{1}{2}}.$$

A rather more general (but still far from rigorous) procedure is to begin from the well-known integration theorem

$$\int \log x \, dx = x \log x - x + \text{constant}.$$

Taking this between the limits 1 to n , we have

$$\int_1^n \log x \, dx = n \log n - n + 1.$$

We can replace the integral by the approximate expression $(x_2 - x_1) \log x_1 + (x_3 - x_2) \log x_2 + \dots + (x_f - x_{f-1}) \log x_{f-1}$, where $x_1, x_2, x_3, \dots, x_f$ are a series of equally spaced values of x ranging from 1 to n , provided any of the differences $x_r - x_{r-1}$ are small compared to the x_r . If n is very large, we can make these differences unity, and thus replace the integral by

$$\log 1 + \log 2 + \dots + \log n.$$

Thus approximately

$$\sum_1^n \log r \doteq n \log n - n + 1$$

$$\doteq n \log n - n.$$

B. The Preponderance of Certain States as Regards the Numbers of Complexions Embraced in Them.—We have seen that in a state in which the distribution of the molecules among the cells is n_1, n_2, \dots, n_c , the “complexion-number” $W(n_1, n_2, \dots, n_c)$ is given by the approximation

$$\log W(n_1, n_2, \dots, n_c) = n \log n - \sum_{r=1}^c n_r \log n_r.$$

We shall denote the expression on the right-hand side by $k(n_1, n_2, \dots, n_c)$. The function $k(n_1, n_2, \dots, n_c)$ has its maximum value when all the n_r are each equal to n/c ; this value we shall denote by k_m . So the maximum value of $W(n_1, n_2, \dots, n_c)$ is W_m where

$$\log W_m = k_m = n(\log n - \log a),$$

a being written for n/c .

To investigate the relative numerical strength of states in the neighbourhood of this state, let us write

$$n_1 = a + \beta_1, n_2 = a + \beta_2, \dots, n_c = a + \beta_c,$$

where $\beta_1, \beta_2, \dots, \beta_c$ are a set of positive or negative integers which must satisfy the relation

$$\sum_{r=1}^c \beta_r = 0.$$

It follows that $k(n_1, n_2, \dots, n_c)$ for this state is connected with k_m by the equation

$$\begin{aligned} k_m - k &= \sum_{r=1}^c \left\{ (a + \beta_r) \log(a + \beta_r) \right\} - n \log a \\ &= \sum_{r=1}^c \left\{ (a + \beta_r) \log(a + \beta_r) - (a + \beta_r) \log a \right\} \\ &= \sum_{r=1}^c \left\{ (a + \beta_r) \log \left(1 + \frac{\beta_r}{a} \right) \right\} \\ &= \sum_{r=1}^c \left\{ (a + \beta_r) \left[\frac{\beta_r}{a} - \frac{1}{2} \left(\frac{\beta_r}{a} \right)^2 + \frac{1}{3} \left(\frac{\beta_r}{a} \right)^3 - \dots \right] \right\} \end{aligned}$$

using the well-known expansion of $\log(1+x)$.

If we work out this expression we obtain a series whose terms are multiples of the expressions $\sum \beta_r$, $\sum \beta_r^2$, $\sum \beta_r^3$, etc. The first term is, of course, zero, and we find after a little rearrangement that

$$\begin{aligned} k_m - k &= \frac{a}{2} \left\{ \sum_{r=1}^c \left(\frac{\beta_r}{a} \right)^2 - \frac{1}{3} \sum_{r=1}^c \left(\frac{\beta_r}{a} \right)^3 + \frac{1}{6} \sum_{r=1}^c \left(\frac{\beta_r}{a} \right)^4 \right. \\ &\quad \left. - \frac{1}{10} \sum_{r=1}^c \left(\frac{\beta_r}{a} \right)^5 + \text{etc.} \right\} \quad (\text{I.}) \end{aligned}$$

For small values of the β_r , the series reduces to its first term, which, being a sum of squares, is essentially positive, as we

should naturally expect since $k_m > k$ for any values of the β_r .

In the text of the chapter, the statement was made that the number of complexions embraced in these states for which the β_r are zero or equal to small fractions of a , are sufficiently great to "swamp" the complexions embraced in states diverging in a perceptible degree from uniformity of distribution. The justification of this depends on equation (I.). On its right-hand side the ratio of the second term to the first is

$$\frac{1}{3} \frac{\sum \beta_r^3}{a \sum \beta_r^2},$$

and if the ratios of the various β_r to a are sufficiently small, this is also small, so that the second and also the subsequent terms of the series can be neglected, and we can write

$$k_m - k = \frac{a}{2} \sum x_r^2,$$

where

$$x_r = \frac{\beta_r}{a}.$$

We thus arrive at the result that if W is the complexion number for the state defined by the integral values $\beta_1, \beta_2, \dots, \beta_c$ for deviation from uniformity, then W satisfies approximately the equality.

$$\begin{aligned} W &= e^k \\ &\doteq \exp \left(k_m - \frac{a}{2} \sum x_r^2 \right) \\ &= W_m \exp \left(- \frac{a R^2}{2} \right) \end{aligned}$$

where

$$R^2 = x_1^2 + x_2^2 + \dots + x_c^2 \quad . \quad (\text{II.})$$

W , of course, only attaining the maximum value W_m where every β_r (or x_r) is zero.

Now let us for the moment turn our attention to the following little problem. Despite its apparent irrelevance, it will soon be apparent why we do so.

Imagine that we have a series of small particles dotted about in space at the points of a regular cubical lattice, and that the mass of any particle is equal to $m e^{-ar^2}$ where r is the distance of the particle from an origin which is itself a point of the lattice, m being the mass of the particle at the origin. If we were required to find the total mass within a sphere of given radius l , and the elementary cubes of the lattice were small enough, a sufficiently accurate answer to the question would be found by supposing the matter to be distributed continuously and not at discrete points, so that the density at a point is given by ρe^{-ar^2} , ρ being the density at the origin. The mass within a sphere l would be

$$4 \pi \rho \int_0^l r^2 e^{-ar^2} dr,$$

which is equal to

$$4 \pi \rho a^{-\frac{3}{2}} \int_0^{la^{\frac{1}{2}}} \xi^2 e^{-\xi^2} d\xi,$$

where

$$\xi = ra^{\frac{1}{2}}.$$

Now we saw in the appendix to the last chapter that the definite integral

$$\int_0^\infty \xi^2 e^{-\xi^2} d\xi$$

is equal to $\pi^{\frac{1}{2}}/4$; it is also true that the whole of this value is practically contributed between the limits 0 to 3; which shows that in our problem almost the entire mass of the lattice of particles is within a sphere whose radius is three times $a^{-\frac{1}{2}}$.

To return, after this digression, to the main argument, the solution of the problem concerning the preponderance of complexions is just a multidimensional analogue of the lattice problem with an analogous answer. A state can be supposed to be represented by a "point" x_1, x_2, \dots, x_c in a c -dimensional space. At the "point" we suppose some entity of magnitude W located. We can then, in order to reduce the mathematical process to an integration, suppose the entity distributed uniformly with a density

$$A \exp \left(-\frac{aR^2}{2} \right)$$

and the amount of the entity within a certain extension of the c -dimensional space can be determined by the integral

$$A \int \int \dots \int e^{-\frac{aR^2}{2}} dx_1 dx_2 \dots dx_c$$

throughout the extension.

The knowledge of integration required is rather outside the usual academic courses delivered to students for whom this book is intended. Those interested will find the necessary material under the heading "Dirichlet's Integrals" in the more advanced texts on mathematical analysis, and the full working out of this problem in Jeans' *Dynamical Theory of Gases*. The upshot is similar to that of our lattice problem. Practically the whole W -magnitude of the entity is within an extension close round the origin, that is where none of the x_r exceed rather small integral multiples of $(2/a)^{\frac{1}{2}}$. Since a is assumed to be a large number, this implies that practically all the complexions possible to the molecular system are concentrated in states for which the β_r are small compared with a , i.e., states in which deviation from uniformity is not marked.

It is true that in the above the approximations which we have made exclude implicitly from the analysis states where there are only a few molecules in some cells, since the particular use of Stirling's theorem is rather wide of the mark for small values of n_r . However, a simple consideration of the original factorial expressions will show how relatively unimportant such states are; and in any case one can use the still closer approximation for $\log n!$, viz., $(n + \frac{1}{2}) \log n - n + \frac{1}{2} \log 2\pi$, and find the conclusion still justified, although the expressions are a little more complicated.

CHAPTER III

THE PROBABILITIES OF THE DIFFERENT STATES OF A SIMPLE MOLECULAR SYSTEM

3.1 **The *à priori* Probability of a Complexion.**—So far we have been confining our attention to the *counting* of complexions. In order to discover the probability of a state, we clearly must know or postulate something about the probabilities of the complexions included in it. But, it must be admitted that here we are faced with one of the most difficult questions in the whole subject. There is nothing novel, however, in such a situation. A satisfactory settlement of the postulates of any of the mathematical sciences has proved to be one of the most difficult tasks, calling for intellectual endowment of no mean order on the part of those who have been the pioneers in this elusive branch of knowledge. Many a young student acquires a really skilful mathematical technique during his school and university years, without being aware of the doubtful nature of some of the processes employed unless hedged round with an array of carefully-phrased conditions. Not that there is in this state of affairs anything calling for severe censure on the part of the educational reformer. It is doubtful whether much good can come from too much immersion in “foundations” on the part of a mind as yet immature. No sane teacher ever dreams of troubling boys and girls with closely-reasoned disquisitions on the postulates of geometry. Certain statements very plausible to the young concerning congruence, parallelism and the like, are accepted at the outset, and a start is made on the deduction of theorems, arousing immediate and practical interest in the minds of the pupils.

The author feels that the situation at this stage of our subject is essentially similar. He surmises that his readers

are more anxious to "see results" as soon as possible, without being worried at the moment with a logical discussion of postulates, which, if they have any element of plausibility about them, will be accepted without demur, especially if they lead to conclusions in agreement with experimental fact. Such *à posteriori* justification may indeed be entirely satisfactory for many; but of course it would not be sound to leave matters in such a condition, and some attempt will be made at a later stage to discuss the basis of the postulates used. This, however, cannot be done until the mathematical expression of dynamical laws has been carried a stage further than is usual in the elementary texts of dynamics.

The fundamental postulate introduced at this stage is that if the various phase-cells have the same magnitude, one aspect of a given molecule is as probable as any other; *i.e.*, it is as likely for its "representative point" in the "phase-diagram" to be in any phase-cell as in any other. There is a certain plausibility about the assumption, which, however, must not blind us to the fact that some time or other it should be subjected to careful scrutiny. Clearly the history of the system is determined by dynamical law, and if our postulate be true, it must at least be a possibility that any molecule can in a sufficiently long lapse of time have been in every cell. In the first chapter the postulate of equal *à priori* probability of each aspect for an article after a throw was based on the fact that repeated throwing does show every aspect for an article in approximately equal numbers during a long time. No such direct experimental evidence comes to our assistance here; we are not on such familiar terms with individual molecules as with coins and dice; nor have we the services of "Maxwell demons" to call upon! However, let us make the assumption for the sake of practical progress now and worry about it later.

Certain obvious reservations must be made in the application of this postulate, however, which call for immediate notice. If the body of which our molecular system is regarded as an analogue, be solid, we find it hard to admit that any molecule can be in any "configuration-cell" into which we

divide the volume, even in long lapses of time. No doubt we can appeal to the experiments of Roberts-Austen and others on diffusion in the solid state ; but still the essence of the molecular picture of a solid is that the molecules, even if they are not fixed in unchanging neighbouring positions relative to one another, are vibrating about the points of some lattice as origins. And if each molecule cannot wander from configuration-cell to configuration-cell at random, neither can its representative point in the phase-diagram roam fortuitously about the phase-cells. This difficulty, however, is not serious. It serves to show that we shall have to treat the solid state on a somewhat different plan to the fluid states where our postulate has a greater air of plausibility. We shall find that in the solid state the interest centres round the vibrations about the set of fixed points and the co-ordinates and velocities of each molecule with reference to its own individual "origin" are the quantities which determine the phase at any definite instant, and it is with regard to partitions of a phase-diagram constructed on such an understanding that our postulate will be introduced.

For the present, therefore, we confine ourselves to the fluid states, and in order to simplify our preliminary considerations we shall begin with the gaseous state where no difficulties will be raised by intermolecular forces. In short, we shall at the outset deal with a monatomic gas.

Another condition which restricts our postulate concerns the question of energy. In partitioning into configuration-cells, a natural limit is placed on the cells of a configuration-diagram by the external surface of the body. In a velocity-diagram no such boundary is obvious, yet dynamical considerations yield one very readily. If a velocity-cell were sufficiently far from the origin, the velocity represented by its central point might be so great that if even a single molecule were possessed of this velocity, its kinetic energy would be greater than the energy-content of the body considered. Thus a sphere of definite radius excludes velocity-cells which cannot come within our consideration. Indeed, instead of appealing to a hard, impenetrable boundary to

limit the configuration-cells, we might adopt a similar method of limitation as for the velocity-cells. That is, conceive that the region occupied by the gas is a region in which a field of force exists whose potential is vanishingly small unless one approaches the boundary, where it rises rapidly as we proceed outwards to values so great, that were even one molecule to be in this external region, its potential energy would exceed the energy-content of the body. Thus we place a natural limit on the phase-cells, to which the postulate of equal *a priori* probability can be applied, by means of one condition, viz., the definite energy-content of the body of which the molecular system is a model.

One other point should be mentioned, before proceeding to definite probability calculations. For a reason which may not appear necessary at present, but which will be recognised as a matter of great convenience later, we will assume that the components of the phase of a molecule will include not the components of its velocity, but of its momentum. Of course, at present, this amounts to nothing more than a change of scale in the phase diagram; but the change will justify itself very decidedly when dealing with more complex systems.

If there are c cells of equal magnitude in the phase-diagram, the probability of a molecular representative point being in one of them, is by the postulate of equal probability equal to c^{-1} ; i.e., in the formula (1.2.4) $p_1 = p_2 = \dots = p_c = c^{-1}$, and the probability of the state (n_1, n_2, \dots, n_c) , would appear to be

$$W(n_1, n_2, \dots, n_c) c^{-n}.$$

But this overlooks the limitation placed upon the total number of possible complexions by energy considerations. If the body of which the molecular system is a model is considered to be at constant temperature, the energy-content is given, and the total number of complexions is not c^n , for many of these would be inconsistent with the equations

$$n_1 + n_2 + \dots + n_c = n. \quad (3.1.1)$$

$$n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_c \epsilon_c = E. \quad (3.1.2)$$

where $\epsilon_1, \epsilon_2, \dots, \epsilon_c$ are the energies of a molecule when its representative point is in the first, second, \dots, c^{th} cell respectively and E is the energy-content of the body. We have to consider the sets of *positive* integers n_1, n_2, \dots, n_c which satisfy (3.1.1) and (3.1.2), and add together the $W(n_1, n_2, \dots, n_c)$ functions for each set. If the sum is s , then s is the total number of *possible* complexions, and the probability of the state (n_1, n_2, \dots, n_c) is

$$\frac{W(n_1, n_2, \dots, n_c)}{s} \quad \dots \quad (3.1.3)$$

These considerations clearly take account of the condition mentioned above which determines the boundary of the possible phase cells; for any cells for which $\epsilon > E$ are excluded automatically by (3.1.2). The quantities ϵ_r are the energies corresponding to the centres of the cells. They will be given by some expression such as

$$\frac{\xi^2 + \eta^2 + \zeta^2}{2m} + \phi(x, y, z),$$

where ξ, η, ζ are the components of *momentum* for the phase, m the mass of the molecule, and $\phi(x, y, z)$ the potential energy of the molecule in the phase, due to any external field of force, such as gravity. For certain phase-cells on the boundary $\phi(x, y, z)$ will also include the potential energy, mentioned earlier, which has an evanescent value in the main portion of the body's volume, but becomes rapidly significant as we approach the external surface, rising to a value greater than E . In the functional form of $\phi(x, y, z)$ will occur certain coefficients entering as factors of the powers and products of x, y, z in the various terms or in some other recognised manner. *E.g.*, the quantity g will occur if gravity is regarded as acting on the molecules. These quantities are called "parameters." They are regarded as constants in investigations on the probabilities of given states for a system with given energy, but, as will appear later, when drawing thermodynamic conclusions from statistical mechanics we have to consider changes in energy-content, and one way of producing such change is by an alteration of parameters, such as is caused by a change

in external bodies producing a field of force or in a movement of the external surface of the body ; this, in fact, being the analogue of " external work " done by or on the system. The reader is reminded that we are at the moment dealing with a gaseous system where intermolecular forces play no part. If it were not so, the energy of the system would include the mutual potential energy of the molecules which would not be proportional to the first power of the concentration and in the expression on the left side of (3.1.2) the ϵ_r could not be regarded as merely functions of the phases and parameters, but would also depend on the values of n_1, n_2, \dots, n_c . In other words, E could not be put equal to a *linear* function of the n_r . This consideration must seriously modify the treatment of liquids as compared with that of gases.

The expression (3.1.3) clearly implies an equal probability for each of the s possible complexions, and we refer once more to the necessity for a closer scrutiny at a later stage of the postulated foundations. This is no matter of repeated random " throwing " of molecules into cells. In casting dice or coins they are gathered up and thrown in a manner subject to no law other than the " law of chance." But even if we imagine that the molecular system is just now in any complexion we like, the subsequent complexions of its history do not follow " by chance," but are the results of movements and collisions subject to the laws of dynamics. Waiving, however, closer investigation of this knotty point for the present, we proceed to discover the state with the maximum probability.

3.2 The State of Maximum Probability.—This will no longer be given by the equality of n_1, n_2, \dots, n_c . The condition (3.1.2) alters the whole character of the solution. As before, we have to find the values of the n_r which will make $W(n_1, n_2, \dots, n_c)$ maximum (for given E, s is also given), but subject to the condition (3.1.2) as well as (3.1.1). Postponing for the moment the details of the solution, it appears that in the most probable state $n_1 = \nu_1, n_2 = \nu_2, \dots$, etc., where

$$\nu_r = C e^{-\mu \epsilon_r} \quad . \quad . \quad . \quad (3.2.1)$$

C and μ being two quantities which are functions of E , n and the parameters. These are determined by the two equations (which are, of course, conditions (3.1.1) and (3.1.2) for this state),

$$C \sum_{r=1}^c e^{-\mu \epsilon_r} = n \quad . \quad . \quad . \quad (3.2.2)$$

$$C \sum_{r=1}^c \epsilon_r e^{-\mu \epsilon_r} = E \quad . \quad . \quad . \quad (3.2.3)$$

Division of (3.2.3) by (3.2.2) gives

$$\frac{\sum \epsilon_r e^{-\mu \epsilon_r}}{\sum e^{-\mu \epsilon_r}} = \frac{E}{n} \quad . \quad . \quad . \quad (3.2.4).$$

Equation (3.2.4) determines μ as a function of the average molecular energy E/n and the parameters, and thereupon (3.2.2) or (3.2.3) will determine C .

When we set out the steps of the solution presently we shall see that, since it follows the usual procedure of determining maxima and minima in the calculus, we are treating the n_r as *continuous* variables for the time being and, of course, there is no guarantee that any of the expressions $C e^{-\mu \epsilon_r}$ are integral. This is one of those minor troubles which beset us when we are engaged in discussing bodies with molecular structure by a mathematical method which practically implies that we are dealing with a continuous medium. The consequences, as we shall see, are in certain connections too serious to be overlooked and will compel us to adopt some form of "quantum hypothesis," but in the present connection we are after all dealing in the main with such large values of n_r that a change of unity while not exactly infinitesimal is relatively so small that the results of introducing the infinitesimal variations of the calculus is not going to lead to serious error. In (3.2.1) we can regard ν_r as such an integer that $C e^{-\mu \epsilon_r}$ lies between ν_r and $\nu_r \pm 1$, if not exactly equal to ν_r . The form of the solution once more excludes certain cells without any appeal to physical boundaries; for if ϵ_r is large enough, $e^{-\mu \epsilon_r}$ is so small that $C e^{-\mu \epsilon_r}$ is a proper fraction. It follows that in (3.2.2) and (3.2.3) the limits of the summations may be

omitted and the series regarded as infinite since beyond a certain term there will be a negligible residue.

A proof exactly on the lines of that in the appendix to Chapter II. can be constructed to show that if we consider the probabilities of states given by

$$n_r = \nu_r + \beta_r$$

then the combined probabilities of the most probable state and those states for which the β_r have relatively small values practically swamp the probabilities of all other states. Thus, *subject to a satisfactory settlement of the doubtful postulate of equal probability of individual complexions in the prolonged history of the gas*, we find that there is a "normal state" of the molecular model in or near which it will always be, except for brief and insignificant intervals of time. It is this state which we clearly must investigate if we are to derive by statistical-mechanical methods the well known thermodynamic properties of a system in *thermodynamic equilibrium*. We shall begin this task in the next chapter, and conclude this one by laying out the proof of the result (3.2.1).

As before we seek the "max-min" condition for $\log W$ regarded as given by the approximation

$$n \log n - \sum_{r=1}^c n_r \log n_r \quad . \quad . \quad . \quad (3.2.5)$$

subject to the conditions (3.1.1) and (3.1.2). As already stated we can without serious error regard the n_r as continuous variables. The method employed is known as the "Method of Undetermined Multipliers," and although not absolutely necessary, a perusal of an exposition of the method in a text of the calculus will prove helpful to any reader not familiar with it.

Let us alter the n_r to $n_r + \delta n_r$, then the variation in $\log W$ is given by

$$\delta \log W = - \sum (1 + \log n_r) \delta n_r \quad . \quad . \quad (3.2.6)$$

and the variations, δn_r , must, on account of (3.1.1) and (3.1.2) satisfy the two equations

$$\sum \delta n_r = 0 \quad . \quad . \quad . \quad (3.2.7)$$

$$\sum \epsilon_r \delta n_r = 0 \quad . \quad . \quad . \quad (3.2.8).$$

But if the values of n_r be such as to make $\log W$ maximum or minimum for any small variations from these values, then the equation

$$\Sigma (1 + \log n_r) \delta n_r = 0,$$

or, by reason of (3.2.7),

$$\Sigma \log n_r' \delta n_r' = 0 \quad . \quad . \quad . \quad (3.2.9)$$

must be true as well as the equations (3.2.7) and (3.2.8).

If λ and μ are *any quantities whatever*, it follows as a matter of course that

$$\Sigma (\log n_r + \lambda + \mu \epsilon_r) \delta n_r = 0 \quad . \quad . \quad (3.2.10)$$

This being so, let us *choose* λ and μ so that

$$\log n_1 + \lambda + \mu \epsilon_1 = 0$$

$$\log n_2 + \lambda + \mu \epsilon_2 = 0$$

This is quite possible; these are two simple simultaneous equations determining the two quantities λ and μ uniquely as functions of $\epsilon_1, \epsilon_2, n_1$ and n_2 ; in fact

$$\mu = \frac{\log n_2 - \log n_1}{\epsilon_1 - \epsilon_2}$$

$$\lambda = -\frac{\epsilon_1 \log n_2 - \epsilon_2 \log n_1}{\epsilon_1 - \epsilon_2}$$

It follows that *with these two values of λ and μ*

$$(\log n_3 + \lambda + \mu \epsilon_3) \delta n_3 + (\log n_4 + \lambda + \mu \epsilon_4) \delta n_4 + \dots \dots \dots$$

$$\text{etc.} = 0 \quad . \quad (3.2.11)$$

This result must be true for *any* values of the variations $\delta n_3, \delta n_4, \dots \dots \dots$; for having chosen any set of them, we can choose δn_1 and δn_2 to satisfy

$$\delta n_1 + \delta n_2 + \delta n_3 + \delta n_4 + \text{etc.} \dots \dots \dots = 0.$$

But this cannot be so unless the individual multipliers of $\delta n_3, \delta n_4, \text{etc.}$, in (3.2.11) are themselves zero, provided, of course, that λ and μ have the values given above. Thus it transpires that in the condition when $\log W$, and therefore W/s , has a maximum or minimum value, the following equations are all true

$$\begin{aligned}
\log n_1 + \lambda + \mu \epsilon_1 &= 0 \\
\log n_2 + \lambda + \mu \epsilon_2 &= 0 \quad . \quad . \quad . \quad (3.2.12) \\
\log n_3 + \lambda + \mu \epsilon_r &= 0 \\
. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\
. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \\
\log n_r + \lambda + \mu \epsilon_r &= 0 \\
. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .
\end{aligned}$$

These equations determine the n_r as functions of the ϵ_r and λ and μ , and if these values are inserted in (3.1.1) and (3.1.2) they determine λ and μ as functions of the ϵ_r , E and n ; and so determine the n_r as functions of the ϵ_r , E and n . In short, c equations, such as (3.2.12) and the equations (3.1.1) and (3.1.2), constitute $c + 2$ simultaneous equations determining uniquely the $c + 2$ quantities $n_1, n_2, \dots, n_c, \lambda, \mu$ in terms of the ϵ_r , E and n . The result is

$$n_r = C e^{-\mu \epsilon_r},$$

where $C = e^{-\lambda}$, and as pointed out above, (3.2.4) will then determine μ and (3.2.2) or (3.2.3) will determine C or λ . Since the equations determining C (or λ) and μ involve *summations over all the cells*, which in practice will amount to integrations throughout the region of the phase-diagram bounded by the energy-condition, C and μ will not depend on individual ϵ_r , *i.e.*, on individual phases, but will be *functions of the parameters* which, in conjunction with the phase, enter into the functional form giving any ϵ_r in terms of $\xi_r, \eta_r, \zeta_r, x_r, y_r, z_r$.

We still have to satisfy ourselves that the corresponding value of W is a maximum and not a minimum. This is almost obvious "on sight," but if any one requires a formal proof, he has only to make a small modification of the analysis in Appendix B to Chapter II. Writing $\nu_r + \beta_r$ for ν_r , we find

$$\begin{aligned}
\log W_m - \log W &= \Sigma \{ (\nu_r + \beta_r) \log (\nu_r + \beta_r) - \nu_r \log \nu_r \} \\
&\text{(and after a few steps on precisely similar lines to those in the appendix)} \\
&= \frac{1}{2} \Sigma \left\{ \nu_r \left[\left(\frac{\beta_r}{\nu_r} \right)^2 - \frac{1}{3} \left(\frac{\beta_r}{\nu_r} \right)^3 + \dots \right] \right\}
\end{aligned}$$

For small values of the β_r , the right-hand side is positive, no matter what the sign of the β_r (for, of course, the ν_r are positive).

Hence $\log W_m > \log W$, and W_m is therefore a maximum and not a minimum. A continuation of the discussion leads as before to the enormous preponderance of the combined probabilities of the normal state and states near it over the combined probabilities of the remaining states.

CHAPTER IV

TEMPERATURE AND THE DISTRIBUTION CONSTANT

4.1 The Average Energy of a Molecule.—When we begin to consider some practicable method of calculating μ and C from equations (3.2.2) and (3.2.3), it is clear that no progress is possible by methods of series summation unless some definite information is available concerning the magnitude of the phase-cell. There is nothing in the so-called “classical” dynamical methods to give us any help in this respect; in fact it is one of the signal benefits which the quantum hypothesis has conferred on our mathematical methods that it has in conjunction with experimental work on spectroscopic phenomena suggested an answer to this difficulty. However, we shall have to defer this matter to a later stage. In the meantime we shall have to convert the series summations into integrations, thus leaving in our expressions an entirely undetermined quantity, which, for many purposes, is no drawback. Thus we shall have to replace a symbol such as n_r by an integral

$$\int \dots \int f(\xi, \eta, \zeta, x, y, z) d\xi d\eta d\zeta dx dy dz,$$

the integration being extended over the r^{th} phase-cell, $f(\xi, \eta, \zeta, x, y, z)$ being some *continuous* function of the variables $\xi, \eta, \zeta, x, y, z$. The solution for the state of maximum probability worked out in the last chapter shows that for ν_r we must write the above integral with the function $f(\xi, \eta, \zeta, x, y, z)$ given the form

$$D \exp \left\{ -\frac{\mu}{2m} (\xi^2 + \eta^2 + \zeta^2) - \mu \phi(x, y, z) \right\}$$

where D is a constant.

Confining ourselves for the moment to the case in which

the gas is free from external force, it follows that ν_r is replaced by

$$D \int \dots \int \exp \{ -a (\xi^2 + \eta^2 + \zeta^2) \} d\xi d\eta d\zeta dx dy dz \quad (4.1.1)^*$$

extended over the r^{th} phase-cell, where $a = \mu/2m$. Further the quantity $\epsilon_r \nu_r$ must be replaced by

$$\frac{D}{2m} \int \dots \int (\xi^2 + \eta^2 + \zeta^2) \exp \{ -a (\xi^2 + \eta^2 + \zeta^2) \} d\xi d\eta d\zeta dx dy dz \quad (4.1.2)$$

also extended over the r^{th} cell.

The equations (3.2.2) and (3.2.3) are now replaced by

$$Dv \iiint \exp \{ -a (\xi^2 + \eta^2 + \zeta^2) \} d\xi d\eta d\zeta = n \quad (4.1.3)$$

$$\frac{Dv}{2m} \iiint (\xi^2 + \eta^2 + \zeta^2) \exp \{ -a (\xi^2 + \eta^2 + \zeta^2) \} d\xi d\eta d\zeta = E \quad (4.1.4)$$

where v is the volume of the system. The summations were over all phase-cells, so that the integrations are now practically from $-\infty$ to ∞ for each variable. Using the results quoted in the appendix to Chapter I. we obtain from (4.1.3)

$$Dv \left(\frac{\pi}{a} \right)^{\frac{3}{2}} = n \quad (4.1.5).$$

To deal with (4.1.4) we first observe that

$$\begin{aligned} & \iiint \xi^2 \exp \{ -a (\xi^2 + \eta^2 + \zeta^2) \} d\xi d\eta d\zeta \\ &= \int_{-\infty}^{\infty} \xi^2 e^{-a\xi^2} d\xi \cdot \int_{-\infty}^{\infty} e^{-a\eta^2} d\eta \cdot \int_{-\infty}^{\infty} e^{-a\zeta^2} d\zeta \\ &= \frac{1}{2} \left(\frac{\pi}{a^3} \right)^{\frac{1}{2}} \left(\frac{\pi}{a} \right)^{\frac{1}{2}} \left(\frac{\pi}{a} \right)^{\frac{1}{2}} \\ &= \frac{1}{2} \left(\frac{\pi^3}{a^5} \right)^{\frac{1}{2}} \end{aligned}$$

* Of course ϵ will involve x, y, z , in the boundary cells where the limiting field of force acts; but since ϵ is very large in these, no practical contribution to the integral is made by such cells.

and so (4.1.4) simplifies to

$$\frac{Dv}{2m} \frac{3}{2} \left(\frac{\pi^3}{\alpha^5} \right)^{\frac{1}{2}} = E \quad . \quad . \quad . \quad . \quad (4.1.6)$$

Hence, dividing (4.1.6) by (4.1.5), we obtain

$$\frac{3}{4m\alpha} = \frac{E}{n}$$

or

$$\mu = \frac{3n}{2E} \quad . \quad . \quad . \quad . \quad (4.1.7)$$

and, in consequence

$$\begin{aligned} D &= \frac{n}{v} \left(\frac{\mu}{2\pi m} \right)^{\frac{3}{2}} \\ &= \frac{n}{v} \left(\frac{3n}{4\pi m E} \right)^{\frac{3}{2}} \quad . \quad . \quad . \quad . \quad (4.1.8) \end{aligned}$$

The result (4.1.7) shows that the "distribution-constant" μ of the system is inversely proportional to the average energy of a molecule, so that if the temperature of the system rises, the distribution of the molecules among the phase-cells in the normal state is altered since μ decreases. Thus there is a direct relation between μ and temperature, and it can be readily obtained by considering the pressure of the gas.

4.2 The Equation of State of a Perfect Gas.—The connection between the pressure of the gas and the velocities of its molecules is a simple one which requires for its derivation no other assumption than the postulate that the directions of the molecular velocities shall be distributed uniformly between all possible directions. A molecule which crosses an element of surface within the gas with a velocity u in a direction making an angle ϕ with the surface, transfers across the surface an amount $m u \cos \phi$ of momentum normal to the surface. Let $N(u, \phi)$ stand for the number of molecules per unit volume which have velocities within infinitesimal limits of u , and directions of motion within infinitesimal limits of the direction ϕ . Of such molecules those that cross the element of surface in unit time lie in a volume

$$A u \cos \phi$$

where A is the element of area. Such molecules therefore transfer normal momentum at the rate

$$A N(u, \phi) m u^2 \cos^2 \phi$$

Summing this for all values of ϕ , and remembering that the average value of $\cos^2 \phi$ is $1/3$,* we find that this rate of transfer of normal momentum across A due to molecules with a velocity u or infinitesimally near it, is

$$\frac{1}{3} A N(u) m u^2$$

where $N(u)$ is the number of molecules *per unit volume* having velocities u or near it.

This is

$$\frac{2}{3} A N(u) \epsilon(u)$$

where $\epsilon(u)$ is the kinetic energy $\frac{1}{2} m u^2$ of a molecule. Summing for all molecules, we find that the rate of transference of normal momentum across the surface A is

$$\frac{2}{3} A \cdot \frac{E}{v}.$$

Thus the pressure is

$$\frac{2}{3} \frac{E}{v}$$

or two-thirds of the energy-density.† Hence if p is the pressure

$$pv = \frac{2}{3} E$$

$$\text{by (4.1.7)} \quad = \frac{n}{\mu} \quad . \quad . \quad . \quad . \quad . \quad (4.2.1).$$

But the well-known equation of state is

$$pv = R\theta \quad . \quad . \quad . \quad . \quad . \quad (4.2.2)$$

* If α, β, γ are the three direction-cosines of any direction with respect to three rectangular axes,

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1,$$

and so

$$\overline{\cos^2 \alpha} = \overline{\cos^2 \beta} = \overline{\cos^2 \gamma} = \frac{1}{3}.$$

† Further remarks on this method of calculating the pressure will be made in section (4.5).

where θ is the absolute temperature and R the gas-constant for the given quantity of gas. Thus a comparison of (4.2.1) and (4.2.2) yields

$$\frac{n}{\mu} = R\theta,$$

and since R is proportional to n (for at the same temperature and pressure the number of molecules is proportional to the volume), we have

$$\mu^{-1} = k\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.2.3)$$

where

$$k = \frac{R}{n}$$

and is called the "gas-constant per molecule."

The simple connection between the distribution-constant and the temperature of the gas is now apparent. Incidentally by (4.1.7)

$$\frac{E}{n} = \frac{3}{2} k\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.2.4)$$

or the average energy of a molecule is 1.5 times $k\theta$.

4.3 Mixtures of Gases.—This identification of the distribution-constant with the inverse temperature is further confirmed by studying statistically the distribution in phase of molecules of different kinds in a vessel.

Let us deal with a mixture of two gases, n molecules of one and n' molecules of the other. Consider a state in which n_1, n_2, \dots, n_c molecules of the first gas are in the c phase-cells; n'_1, n'_2, \dots, n'_c of the second also in the same phase-cells. Now such a state can be produced by associating any complexion of the (n_1, n_2, \dots, n_c) state of the first gas with any complexion of the $(n'_1, n'_2, \dots, n'_c)$ state of the second. Thus the number of complexions embraced by the $(n_1, n_2, \dots, n_c, n'_1, n'_2, \dots, n'_c)$ state of the mixture is the product of the separate complexion-numbers for each gas. That is

$$W(n_1, n_2, \dots, n_c, n'_1, n'_2, \dots, n'_c) = \frac{n!}{n_1! n_2! \dots n_c!} \frac{n'!}{n'_1! n'_2! \dots n'_c!}$$

and by the Stirling approximation

$$\log W = n \log n + n' \log n' - \left\{ \Sigma n_r \log n_r + \Sigma n'_r \log n'_r \right\} \quad (4.3.1)$$

To find the normal state we must determine the values of the n_r and n'_r , giving a maximum value to $\log W$ subject to the conditions

$$\Sigma n_r = n \quad . \quad . \quad . \quad . \quad (4.3.2)$$

$$\Sigma n'_r = n' \quad . \quad . \quad . \quad . \quad (4.3.3)$$

and $\Sigma \epsilon_r n_r + \Sigma \epsilon'_r n'_r = E \quad . \quad . \quad . \quad . \quad (4.3.4)$

where E is the energy of the mixture. Careful attention should be paid to the form of condition (4.3.4). We have not *two* energy conditions

$$\Sigma \epsilon_r n_r = \text{constant}$$

$$\Sigma \epsilon'_r n'_r = \text{constant}$$

for the energy of any one component of the mixture does not remain constant. The intermolecular collisions involve a perpetual exchange of energy between the molecules irrespective of the group to which they belong, and so the energy condition is expressed in *one* equation not two. It is this feature of the equations which is responsible for the important result which we shall deduce presently. (There is in general no equality between the energy of one type of molecule in a given phase and that of the other type in the same phase since

$$\epsilon_r = \frac{\xi_r^2 + \eta_r^2 + \zeta_r^2}{2m}$$

and

$$\epsilon'_r = \frac{\xi_r'^2 + \eta_r'^2 + \zeta_r'^2}{2m'}$$

quite apart from considerations of potential energy.)

On proceeding to the solution of the problem on the same lines as before, we find we have to satisfy

$$\Sigma (1 + \log n_r) \delta n_r + \Sigma (1 + \log n'_r) \delta n'_r = 0$$

$$\Sigma \delta n_r = 0$$

$$\Sigma \delta n'_r = 0$$

$$\Sigma \epsilon_r \delta n_r + \Sigma \epsilon'_r \delta n'_r = 0$$

Using the method of undetermined multipliers we multiply the second equation by λ , the third by λ' , and the fourth by μ and add. The $2c + 3$ quantities, viz., the "normal" values of the n_r and n_r' and λ , λ' , μ are determined from (4.3.2), (4.3.3), (4.3.4) and the $2c$ equations

$$\log n_r + \lambda + \mu \epsilon_r = 0 \quad . \quad . \quad (4.3.5)$$

$$\log n_r' + \lambda' + \mu \epsilon_r' = 0 \quad . \quad . \quad (4.3.6)$$

($r = 1, 2, \dots, c$ consecutively).

It is to be noted that, for the reason mentioned, the same μ occurs in the c equations (4.3.5), as in (4.3.6), although not the same λ . These equations yield the normal values, $n_r = \nu_r$ and $n_r' = \nu_r'$ where

$$\nu_r = C e^{-\mu \epsilon_r}$$

$$\nu_r' = C' e^{-\mu \epsilon_r'}$$

C being $e^{-\lambda}$ and C' , $e^{-\lambda'}$; C , C' and μ are, of course, worked out in detail in terms of E , n , n' , and the parameters involved in the ϵ_r and ϵ_r' by means of (4.3.2), (4.3.3), (4.3.4).

Thus the presence of one gas does not upset the nature of the normal distribution of the other, and, as a significant fact, the same value of distribution-constant appears in the normal state of each part. The methods of sections (4.1) and (4.2) are once more applicable, and we find that the average energy of any molecule *irrespective of type* is as before, $1.5 \mu^{-1}$ and the temperature is $(k\mu)^{-1}$.

If the two molecular systems were in separate enclosures they would for an extremely large part of their history be distributed in or near the normal state, but not necessarily with the same distribution-constant. However, on mixing them, their normal state now involves a common-distribution-constant. This statistical deduction, which as we have seen is derived from the dynamical principle of the conservation of energy, is the analogue of the attainment of a common temperature by two gases on mixing. The statistical result can clearly be extended to a gaseous mixture of any number of different gases.

In this connection Avogadro's hypothesis can be readily deduced from these results. Since the two gases at the same

temperature have the same distribution-constant for their normal states, it appears from (4.2.3) that they have the same k . Therefore, the gas constants, R , for two quantities of each gas, each quantity containing the same number of molecules, have equal values. But this amounts to saying that equal volumes of two gases at the same temperature and pressure contain equal numbers of molecules. For a gram-molecule of any gas, R is known to have the value 8.32×10^7 ; and the number of molecules in a gram-molecule is known to be 6.06×10^{23} . Hence the value of k the gas-constant per molecule, is 1.37×10^{-16} .

From (4.2.4)

$$E = \frac{3}{2} R\theta,$$

and so the specific heat of a monatomic gas at constant volume is $3 R/2$.

4.4. Potential Energy.—If an external field of force (other than the one postulated to limit the size of the gas) is acting on the molecules, the integrations carried out in section (4.1) require some little modification, since ϵ is now the sum of $(\xi^2 + \eta^2 + \zeta^2)/2m$ and a function $\phi(x, y, z)$, and the equations (4.1.3) and (4.1.4) become

$$D \iiint e^{-\mu\phi} dx dy dz. \iiint \exp \left\{ -\alpha (\xi^2 + \eta^2 + \zeta^2) \right\} d\xi d\eta d\zeta = n \quad (4.4.1)$$

$$D \int \dots \int \phi e^{-\mu\phi} dx dy d\xi d\eta d\zeta$$

$$+ D \iiint e^{-\mu\phi} dx dy dz. \iiint \frac{\xi^2 + \eta^2 + \zeta^2}{2m} \exp \left\{ -\alpha (\xi^2 + \eta^2 + \zeta^2) \right\} d\xi d\eta d\zeta = E \quad (4.4.2)$$

The first integral in (4.4.2) is the potential energy of the whole gas in the external field of force. Call this Φ . Also represent the integral

$$\iiint e^{-\mu\phi} dx dy dz$$

throughout the whole volume of the gas by the symbol F . Then in (4.1.5) and (4.1.6) we replace D by DF and E by $E - \Phi$; so (4.1.7) is replaced by

$$\mu = \frac{3n}{2(E - \Phi)},$$

so that μ^{-1} is still equal to two-thirds of the average *kinetic* energy of a molecule and the relation between the temperature and the average kinetic energy is not disturbed. The existence of the field does not affect the distribution of the velocities among the molecules ; it does, however, produce lack of uniformity in the density of molecular concentration, since the density in a small volume surrounding the point (x, y, z) is proportional to

$$\exp\{-\mu \phi(x, y, z)\}$$

and thus decreases as we move to places of higher potential. The reader should rightly appreciate these statements. In a region at high potential there are not, of course, in the normal state, as many molecules within certain limits of velocity as in an equal sized region at a low potential ; but the ratio of the numbers of molecules within two defined extensions-in-velocity in a given volume is unaltered by the field of force.

4.5 Some Remarks on Pressure.—The method of calculating the pressure in section (4.2) is probably familiar to the reader, who has no doubt already met it in some textbook of physics. Nevertheless some further discussion of it may not be out of place here, although it might have produced a rather long digression in section (4.2) from the main object of the chapter.

It should be realised, of course, that the transference of *normal* momentum is not to be considered as only from one side of the element of area A to the other ; that would only have given half the pressure. Calling the two sides of the area a and b , we have to estimate the components of momentum normal to the area towards b transferred from side a to side b per unit time, and the components towards a transferred from b to a . These two parts are of course equal in statistical equilibrium, and their sum is the pressure. The procedure can be related very easily to the usual definition of pressure as force per unit area ; for if we conceive a physical surface situated in the interior of the gas, molecules

moving up to the surface and those which have just rebounded from it correspond to the two streams of molecules for an element of area parallel and near to the surface, and the algebraic change of momentum in a given time produced by the surface is the arithmetical sum of the normal momentum-components towards the surface for the oncoming molecules and normal components away from the surface for the receding molecules.

In view of similar considerations arising later in connection with liquids, it is very necessary to be quite clear in each particular illustration as regards the meaning to be attached to the word "pressure." Besides the idea of rate of transference of normal momentum, there is the familiar notion of "hydrostatic pressure" as force per unit area on a surface arising from a "body" force, such as gravity being exerted on each element of the fluid. It should be obvious that so far we have not had much to do with that conception. In any case if it is a question of a relatively small quantity of enclosed gas, its weight is negligible in the treatment of its pressure, since it merely produces a small excess in the pressure exerted by the bombarding molecules on the lower part of the flask over that on the upper, because of the slightly larger density. Of course in the treatment of our atmosphere as a whole, the two ideas lead to the same value; for it is the earth's gravitational attraction which holds our atmosphere to it and as the pressure (in the "bombardment sense") vanishes at its outskirts, its pressure at lower levels is just equal to its hydrostatic pressure, estimated in the elementary way as weight exerted on unit area.

It is, however, in the case of a liquid that serious confusion will arise unless care be taken. As we shall see later, the notion of an "internal" or "intrinsic" pressure due to transference of momentum across an element of area in the interior arises in theoretical discussion just as in the case of a gas; but on account of the larger density this pressure is relatively enormous, and we have no *direct* experience of it. When we use the phrase "pressure of a liquid," we refer, as a rule, to the hydrostatic pressure arising from its weight

and varying markedly with depth in the liquid. But as a matter of fact we shall see later that in the statistical discussion of the liquid state the symbol p is not even used to represent this magnitude either, but is rather associated with the pressure of the saturated vapour of the liquid. In due course we shall see why this is so, and also how it comes that the relatively great internal pressure is not capable of direct experimental detection.

There is in the case of a gas an interesting and instructive way of connecting pressure regarded as rate of transference of normal momentum per unit area and pressure regarded as force per unit area. It will be recalled that, instead of considering a physical boundary to a quantity of gas, we imagined a field of force acting normally inward on the gas molecules at its external layer. We also saw in the last section that if $\phi(x, y, z)$ is the value of the potential energy of a molecule in this field at the point (x, y, z) , then the density of the gas at this point is ρ where

$$\rho = \rho_0 e^{-\mu\phi}$$

ρ_0 being the uniform density of the gas throughout its volume with the exception of the exterior layer referred to. Now it is proved in text-books of hydromechanics that if p stands for the pressure of a fluid in the hydrostatic sense, then p is a function of position which is connected with the body-force by the following equations

$$X = -\frac{1}{\rho} \frac{\partial p}{\partial x}$$

$$Y = -\frac{1}{\rho} \frac{\partial p}{\partial y}$$

$$Z = -\frac{1}{\rho} \frac{\partial p}{\partial z}$$

where X, Y, Z are the components of the body force *per unit mass* of the fluid. Since X, Y, Z vanish in the interior of the gas, the hydrostatic pressure, p , is uniform throughout it. In the layer, however,

$$X = -\frac{1}{m} \frac{\partial \phi}{\partial x}, \text{ etc.,}$$

m being the mass of a molecule, and so

$$\begin{aligned}\frac{\partial p}{\partial x} &= -\frac{\rho}{m} \frac{\partial \phi}{\partial x} \\ &= -\frac{\rho_0}{m} e^{-\mu\phi} \frac{\partial \phi}{\partial x}, \text{ etc.}\end{aligned}$$

Hence

$$p = \frac{\rho_0 e^{-\mu\phi}}{m \mu},$$

the constant of integration being zero since p vanishes as ϕ approaches infinity. Hence in the interior of the liquid, where ϕ is zero,

$$p = \frac{\rho_0}{m \mu}$$

or

$$pv = \frac{n}{\mu}$$

where n is the number of molecules in volume v . But this is just the same equation as (4.2.1) where p , however, represented pressure in the sense of rate of transference momentum.

Equation (4.2.1) shows that if \bar{u}^2 is the mean of the squared velocities of the molecules, then

$$p = \frac{1}{3} \rho \bar{u}^2$$

since $E = \frac{1}{2} \Sigma mu^2 = \frac{1}{2} \rho v \bar{u}^2$.

Thus the "mean squared velocity" is equal to $(3 p/\rho)^{\frac{1}{2}}$, and so is of the same order of magnitude as the velocity of sound through the gas; for the latter is known to be $(\kappa p/\rho)^{\frac{1}{2}}$ where κ is the ratio of the specific heat at constant pressure to that at constant volume, and is between 1 and 1.66 in value. For hydrogen at 0° C., the mean squared velocity is 1,840 metres per second, for oxygen 460 metres per second, etc., varying in fact inversely as the square root of the density under standard conditions or inversely as the square root of the molecular weight.

CHAPTER V

EXTENSION TO MORE COMPLEX MOLECULES

5.1 Equipartition of Energy.—Without the assistance of general dynamical theory, any treatment of molecules which are endowed with a structure must in the nature of things be inadequate. However, the author's aim being to introduce the reader to statistical results of general interest with as little delay as possible, leaving a more thorough treatment to a later stage, we shall make shift to consider the case of complex molecules with the aid of a simple model which has rendered yeoman service in the past to students not too well equipped with mathematical artillery.

Let us regard each molecule as containing within itself "oscillators," *i.e.*, particles attracted by elastic forces towards centres, where they would remain in relative equilibrium with respect to the general body of the molecule. The restoring force is supposed in each case to be proportional to the displacement of the oscillator from its centre in the molecule and so the oscillation is harmonic. Let q stand for the displacement; the velocity of this displacement, dq/dt , is represented by \dot{q} and the acceleration, d^2q/dt^2 , by \ddot{q} . If a is the mass of the particle and bq the restoring force, then the equation of motion is

$$a\ddot{q} + bq = 0$$

and the solution of this is

$$q = A \sin (\omega t - \theta),$$

where ω is equal to $(b/a)^{\frac{1}{2}}$ and is called the "pulsance" ($2\pi \times$ frequency) of the motion. A is the amplitude of the vibration, and θ is the "epoch-angle" determined by the fact that at times $t = \theta/\omega$, $\theta/\omega \pm \pi$, $\theta/\omega \pm 2\pi$, etc. the

displacement is zero. The kinetic energy is $\frac{1}{2} a \dot{q}^2$ and the potential energy is $\frac{1}{2} b q^2$. The total energy is therefore

$$\frac{1}{2} b A^2 \sin^2 (\omega t - \theta) + \frac{1}{2} a A^2 \omega^2 \cos^2 (\omega t - \theta),$$

or $\frac{1}{2} a A^2 \omega^2$. The momentum $a \dot{q}$ we shall represent by the symbol p .

The amplitude and the epoch-angle are not determined by the equation of motion; they depend on the so-called initial conditions; *e.g.*, in the case of a simple pendulum, while the time of swing is determined by the length and intensity of gravity, the amplitude and the actual instant at which the string has an assigned inclination are arbitrary. A and θ are, in fact, two arbitrary integration constants which enter the solution during the integration of the equation of motion. Physically this means, as regards the oscillator, that A and θ have definite values during a free path of the molecule which contains it, but are altered at every encounter between this molecule and any other. In any free path of a molecule the internal oscillator is engaged in a harmonic oscillation with a definite pulsance ω , but with an amplitude and epoch-angle which varies ~~from~~ free path to free path. To make this more obvious we may consider a molecule as a frame of reference for the oscillator. The set of axes with reference to which we estimate q are fixed in the molecule. (For the moment we are regarding the oscillator as having one "degree of freedom," *i.e.*, vibrating to and fro parallel to one axis). As long as the frame of reference is moving with a uniform velocity, the oscillation is not interfered with; at time t

$$\begin{aligned} q &= A \sin (\omega t - \theta) \\ \dot{q} &= A \omega \cos (\omega t - \theta). \end{aligned}$$

An encounter produces an acceleration in the molecular frame of reference for a brief time. This is equivalent to a force acting on the oscillator for the same time in the

opposite direction. We are here appealing to the well known mechanical aspect of the relativity principle. We have only to consider our experiences in a carriage, which has been moving steadily and is then suddenly accelerated or retarded, in order to realise the situation. The oscillator suddenly receives an impulse in a direction opposite to that on the molecule. When it is over, the state of affairs is such that the oscillator has practically the same q but a different \dot{q} and for the subsequent spell of harmonic motion before the next shock, q and \dot{q} cannot be given by the equations above, but by two such as

$$\begin{aligned} q &= A' \sin (\omega t - \theta') \\ \dot{q} &= \omega A' \cos (\omega t - \theta') \end{aligned}$$

with a different A and θ , but, of course, with the same pulsance as before. Hence at every collision not only is the kinetic energy of the molecule changed, but also the internal energy of the oscillator also. The collisions, in short, effect an exchange of energy of translation between the molecules and also between this energy and the internal energies of the molecules.

We can as before bring this new "degree of freedom" within our considerations of probability. The phase of a molecule is now determined by *eight* components, $x, y, z, q, \xi, \eta, \zeta, p$, and an extension-in-phase by the limits x to $x + \delta x, \dots, q$ to $q + \delta q, \xi$ to $\xi + \delta \xi, \dots, p$ to $p + \delta p$. The phase-diagram is now an eight-dimensional one; or if it is preferred, it can be visually represented by four plane diagrams, a point in the fourth one representing q and p . A phase is represented by a "point" in the phase-diagram or a four-point group in the four plane diagrams. A phase-cell can be pictured if one likes, as a group of four elementary rectangles and a "path" as a group of four curves.

If now one "aspect" of a molecule is as possible as any other with this extended notion of aspect, the probability of a state in which n_1 representative points are in the first cell, etc., is as before given by the quotient of W (n_1, n_2, \dots, n_c) by the total number of complexions consistent with the energy condition. The procedure is just as before;

the state of maximum probability is given by equations (3.2.1), (3.2.2), (3.2.3), where ϵ is defined to be

$$\frac{\xi^2 + \eta^2 + \zeta^2}{2m} + \frac{p^2}{2a} + \phi(x, y, z) + \frac{1}{2}bq^2,$$

and involves the phase (q, p) and parameters (a, b) of the internal motion. The same type of proof also serves to show that this state and those very near it constitute the normal state of the system of molecules.

5.2 Partition of Energy.—On reverting to the procedure of section (4.1), we can easily obtain average values for the various parts of the kinetic energy of a molecule which are, as we say, associated with its various degrees of freedom.

In the first place the equation (4.1.3) is replaced by

$$D \int \dots \int e^{-\mu\epsilon} dx dy dz dq d\xi d\eta d\zeta dp = n \quad (5.2.1)$$

In the absence of an external field this reduces to

$$Dv \int e^{-a\xi^2} d\xi \int e^{-a\eta^2} d\eta \int e^{-a\zeta^2} d\zeta \int e^{-\beta q^2} dq \int e^{-\gamma p^2} dp = n$$

where the integrations are practically from $-\infty$ to $+\infty$ in each case * and

$$a = \frac{\mu}{2m}, \beta = \frac{1}{2}\mu b, \gamma = \frac{\mu}{2a}.$$

We thus have

$$Dv \left(\frac{\pi}{a}\right)^{\frac{3}{2}} \left(\frac{\pi}{\beta}\right)^{\frac{1}{2}} \left(\frac{\pi}{\gamma}\right)^{\frac{1}{2}} = n \quad (5.2.2)$$

The kinetic energy associated with the motion of a molecule parallel to the axis of x is $\xi^2/2m$, and so the average of this over every molecule at any moment is

$$\frac{D}{2m} \int \dots \int \xi^2 e^{-\mu\epsilon} dx \dots dp$$

divided by n ; i.e.,

$$\frac{Dv}{2m} \int \xi^2 e^{-a\xi^2} d\xi \int e^{-a\eta^2} d\eta \dots \int e^{-\gamma p^2} dp$$

* See Note 1 to this chapter.

divided by the expression on the left-hand side of (5.2.2). This is equal to

$$\begin{aligned} & \frac{1}{2m} \cdot \frac{\int_{-\infty}^{\infty} \xi^2 e^{-a\xi^2} d\xi}{\int_{-\infty}^{\infty} e^{-a\xi^2} d\xi} \\ &= \frac{1}{2m} \cdot \frac{1}{2} \left(\frac{\pi}{a^3} \right)^{\frac{1}{2}} \bigg/ \left(\frac{\pi}{a} \right)^{\frac{1}{2}} \\ &= \frac{1}{4m a} \\ &= \frac{1}{2\mu}. \end{aligned}$$

A similar result follows for the average of $\eta^2/2m$ and $\zeta^2/2m$, and also for the average of the part of the kinetic energy $p^2/2a$ associated with the internal movement.

The reader should carefully note the meaning of the word "average" in this connection. No statement is made about the average total or partial energies of an individual molecule over a finite lapse of time. We cannot follow individual histories. The "equipartition law" is concerned with energies averaged over all the molecules at any one instant.

The modification introduced into the treatment of pressure in section (4.2) owing to the considerations of internal structure is easily dealt with. It is not difficult to see that the pressure is now two-thirds of the density of the kinetic energy of translation of the molecules (not of the whole kinetic energy); so by the result just obtained

$$p = \frac{2}{3} \cdot \frac{n \frac{3}{2\mu}}{v} *$$

or
$$pv = \frac{n}{\mu}$$

where p is the pressure. As before, this result leads to the

* p is here the pressure and must not be confused with the momentum of an oscillator.

identification of the distribution constant μ with $(k\theta)^{-1}$, where k is the gas constant per molecule.

Indeed the reader should have no difficulty in seeing that the line of proof used can be extended to molecules with oscillators having more than one degree of freedom, *i.e.*, free to vibrate in all directions with reference to axes fixed in the molecule with three degrees. Furthermore, molecules containing more than one oscillator, each oscillator having its own distinctive mass and force-constant, can also be brought within the ambit of the proof. And lastly mixtures of different molecules can be treated in a similar manner to that used in section (4. 3).^{*} The striking feature is the appearance of the same distribution constant in the exponential factor of the distribution law, and this as we have seen, is the result of the liberty of exchange of energy between all the degrees of freedom of the molecules as a whole and of the internal oscillators. The equality between μ^{-1} and $k\theta$ is still maintained and the average kinetic energy associated with any degree of freedom is as before $\frac{1}{2} k\theta$. If p, p', p'', \dots are the partial pressures of the constituent gases, then

$$pv = \frac{n}{\mu} = nk\theta$$

$$p'v = n'k\theta$$

etc.

where n, n', \dots are the numbers of each type of molecule present, this being the familiar law of partial pressures.

It is very necessary to observe that the equipartition law has been confined to average *kinetic* energies, and it is easy to see that the restriction is connected with the fact that the kinetic energy of each molecule is the sum of terms each of which depends on the *square* of a momentum, involving in the proof the possibility of splitting a certain part of the expression $e^{-\mu u}$ into separate factors of the type $e^{-\alpha \xi^2}, \dots, e^{-\gamma p^2}$. It is true that this is just as much a feature of the potential energy of the oscillator in a molecule, which is given by a term involving the square of a co-ordinate; and

^{*} See Note 2 at the end of the chapter.

we can prove just as before that the average potential energy of a harmonic oscillator is also $\frac{1}{2} k\theta$ for each degree of freedom. But in general potential energy is not given by simple square terms. If the restoring force on the oscillator were not proportional to q , the oscillator would be "anharmonic," and the potential energy would not be represented by $\frac{1}{2} b q^2$ and the equipartition proof would fail for it. Also, as regards the external field of force, the potential energy function $\phi(x, y, z)$ is not in general a sum of squares and, again the proof would fail in this connection. For example, if it were a uniform field parallel to the axis of x , the potential energy would be proportional to the x -co-ordinate (choosing the origin at a suitable level) and writing Ax for $\phi(x, y, z)$ we would obtain the average potential energy by dividing

$$\text{DA} \int_0^\infty x e^{-\mu Ax} dx \int \dots \int e^{-\mu \epsilon'} dy dz dq d\xi d\eta d\zeta dp$$

by

$$\text{D} \int_0^\infty e^{-\mu Ax} dx \int \dots \int e^{-\mu \epsilon'} dy dz dq d\xi d\eta d\zeta dp$$

where $\epsilon' = \epsilon - Ax$.

This is

$$\frac{A \int_0^\infty x e^{-\mu Ax} dx}{\int_0^\infty e^{-\mu Ax} dx},$$

which is equal to

$$\frac{A (\mu A)^{-2}}{(\mu A)^{-1}}$$

i.e., μ^{-1} or $k\theta$, just twice the average kinetic energy. In fact, if the potential energy were proportional to any power of x , say x^n , then it can be easily deduced that the average potential energy would be $k\theta/n$. As a general rule, even such relatively simple expressions as sums of powers of the co-ordinates do not hold sway, and so the reader must be careful in the use of the equipartition law, unless applied to kinetic energy. Later, when we reach a fuller dynamical treatment, we shall see that there is a general partition law which covers the equipartition of kinetic energy and gives

us some idea as to procedure in other cases. All this is, of course, based on classical dynamical laws. Wider considerations involving the quantum hypothesis will modify even this general law.

We cannot leave the subject of complex molecules even at this stage without some reference to molecules involving more than one atom. A familiar picture for certain diatomic molecules is that of a dumbbell—two separate atoms held rigidly together. This picture introduces new degrees of freedom connected with rotation as distinct from translation. The student may naturally remark that rotation is just as much a possibility for monatomic molecules as for a diatomic and should therefore have been considered earlier. The answer to this is to draw the reader's attention to an implicit assumption in the model of a monatomic molecule used hitherto. It has been regarded as dynamically equivalent to a hard smooth sphere. The mutual forces exerted at encounters are normal to the surface, and passing through the centre produce no change in rotational momentum nor in the *individual* rotational energies of the molecules. Thus *rotational energy is not exchanged* between molecule and molecule at an encounter, and since it therefore makes its appearance in the equation (3.1.2) as a constant, it does not appear at all in (3.2.8). But it is otherwise for a dumbbell-shaped particle; the forces between the atoms of different diatomic molecules will not produce any change in the component of rotational momentum around the axis of figure, but will do so about any axis at right angle to the figure-axis. This amounts to excluding one of the three new degrees of freedom.* Again we must anticipate later dynamical work when we state that each effective degree brings in on the average $\frac{1}{2} k\theta$ of *kinetic* energy of rotation. Of course, for a less symmetrical diatomic molecule or for a polyatomic molecule, provided we can regard it as rigid, we should have to take into account three degrees of freedom for rotation. These remarks have an important bearing on the specific

* The reader is reminded that rotational velocity about any axis can be resolved into three component angular velocities about three Cartesian axes of reference.

heat of a gas. If the gas be monatomic, with no internal degrees of freedom, the energy-content will be $1.5 nk\theta$, and so the heat capacity *at constant volume* will be $3R/2$ where R is the gas-constant for the amount of gas considered. This is in good agreement with facts. For a diatomic gas we would expect $k\theta$ more energy on the average in a molecule, and this would lead to $5R/2$ as the heat-capacity. For more complex rigid molecules we would expect a still further $\frac{1}{2} k\theta$ of energy per molecule involving $3R$ as the value of the heat-capacity. Provided temperatures are not too low or too high, several gases show good agreement with these results. Thus from elementary thermodynamical reasoning we know that the heat-capacity of a quantity of gas at constant pressure is greater by R than the heat-capacity at constant volume, and so the ratio of the two specific heats for diatomic gases should be $7/5$ or 1.4 , and for more complex gases $4/3$ or 1.33 , two results which are in good agreement with the facts for some gases. But as diatomic gases are reduced in temperature, it is found that their specific heat per gram-molecule falls asymptotically to the values for monatomic gases, from which it would appear that for some reason not evident in the classical dynamical treatment, the rotational energy has on the average a value progressively smaller and smaller than the amount $k\theta$ per molecule. This is a discrepancy which, as we shall see later, involves the use of the quantum hypothesis to remove. At high temperatures the specific heats show signs of attaining higher values than those theoretically deduced. To account for this we have to abandon the restriction as to rigidity in the molecule and admit that the molecule may have kinetic energy arising from the relative vibrations of its constituent atoms and potential energy arising from relative displacements. But again we have the same difficulty to meet. The classical treatment does not show why these energies of internal vibration and strain should not make their appearance at normal temperatures. So long as elastic strain of the parts of the molecule are postulated the relative partition of the total energy among the various degrees of freedom is settled not by the particular value of μ , but by the expression for

the energy of a molecule in terms of its co-ordinates and momenta (external and internal). Thus for all "squared terms" there is partition on an equality basis; and for other terms though not so simple, it is definite. Nor is this all. The facts of the spectral lines of gases show that there is a quite complicated vibrational mechanism within every atom and molecule which is the dynamical equivalent of numerous oscillators. Why then should the specific heat of any gas not be very much greater than it really is? On any reasonable assumption in addition to the half-dozen or so energy-quantities of $\frac{1}{2} k\theta$ assigned to each molecule, there should be many more for the internal degrees of freedom of the radiating mechanism. Again these discrepancies can only be dealt with by an appeal to some form of quantum theory and there we must leave it for the present.

NOTE 1.—Since the oscillator must in its vibration be confined within the molecule, it may appear absurd to integrate for q from $-\infty$ to $+\infty$. Actually it is not inconsistent with our knowledge of the sizes of atoms and molecules to conceive that a displacement of the oscillator is quite possible which renders the potential energy very much greater than the average value $(2\mu)^{-1}$; for such a displacement $e^{-\beta q^2}$ would have reached such a minute value that the part of the integral between this value and infinity is negligible. A similar remark applies to the p integration.

NOTE 2.—A slight difficulty in the mathematics may present itself to the reader in connection with the fact that the number of oscillators or degrees of freedom within a molecule of one type in the mixture may not be the same as the number within a molecule of another type; so that we cannot apparently use a common set of phase-cells for each group of molecules, the dimensionality being different in

each case. Formally we surmount the difficulty easily by bringing the number of oscillators in every molecule up to the same value. We can then conceive the "extra" oscillators in those molecules which have really less than the maximum number to possess zero mass and so to contribute no energy to the total amount.

CHAPTER VI

THE SECOND LAW OF THERMODYNAMICS

6.1 The Normal State of a Molecular System and Thermodynamic Equilibrium.—In accordance with our aim of bringing out the connection between statistical mechanics and thermodynamical facts as soon as possible, we propose in this chapter to deduce the second law of thermodynamics for a gas from the results hitherto obtained, before proceeding to a further development of the subject itself.

We have seen that the molecular system is, if our probability-postulate be accepted, for a relatively great part of its history in or extremely near to the “normal” state defined by the c equations

$$\nu_r = C e^{-\mu \epsilon_r}$$

or

$$\log \nu_r = \lambda - \mu \epsilon_r \quad . \quad . \quad . \quad . \quad . \quad (6.1.1)$$

where λ is written for $\log C$. (For convenience a change of sign in λ from the earlier sections is made.) These, combined with

$$\sum_{r=1}^c \nu_r = n \quad . \quad . \quad . \quad . \quad . \quad (6.1.2)$$

$$\sum_{r=1}^c \epsilon_r \nu_r = E \quad . \quad . \quad . \quad . \quad . \quad (6.1.3)$$

serve to determine the ν_r , λ and μ as functions of E , n and the parameters which we shall denote by the symbols a_1, a_2, \dots, a_e . Let us change our point of view a little and regard (6.1.1), (6.1.2) and (6.1.3) as equations determining the ν_r , E and λ as functions of μ and the parameters. That is, we are going to consider the molecular system passing from the *normal* state for one value of μ to the normal

state for another value of μ , involving, of course, changes in the energy E , as well as in λ and the individual ν_r or normal numbers in each phase-cell. Remember that μ has no meaning for the molecular system apart from the normal state. If the system be not in the *normal* state, it is a direct result of our postulate that it will gradually tend to it. There is no dynamical impossibility involved in a statement that there might be abnormal states of distribution in which the system might remain for ever. All we can say is that on our probability basis it is enormously improbable. It is not impossible that all the peoples of the world could be on the Isle of Man in one day (actually a density of one person per square yard would just about suffice) but—well! the point need not be laboured.

The analogy between this normal state and the state of thermodynamic equilibrium of an isolated physical system is too obvious to escape notice, and the analogy is very close indeed; for from the equations of the normal state we can construct functions of μ and the parameters which are as a matter of pure mathematics connected by differential equations of precisely the same form as those which are found by experiment to connect those functions of the thermodynamic variables of a system which we call the internal-energy-function, the free-energy-function, and the entropy-function. The proof which follows is, to be sure, limited at the moment to gaseous systems; but it is surprising how little further elaboration of mathematical detail is required when we deal with this question for other systems at a later stage.

6.2 The Entropy Law.—On solving (6.1.1) (6.1.2) (6.1.3) we express the ν_r as functions of $\mu, a_1, a_2, \dots, a_e$ (remembering that $\epsilon_1, \epsilon_2, \dots, \epsilon_e$ are functions of a_1, a_2, \dots, a_e). Inserting these in (6.1.3) we obtain a function of $\mu, a_1, a_2, \dots, a_e$, which is equal to E ; we shall denote it by

$$H(\mu, a_1, a_2, \dots, a_e)$$

or briefly by

$$H(\mu, a).$$

Also from (6.1.1) we express λ as a function of the μ and the

a_r . Let us write for $n \lambda/\mu$ the functional form $\Psi(\mu, a_1, a_2, \dots, a_e)$, or

$$\Psi(\mu, a) = \frac{n \lambda}{\mu}.$$

Suppose the molecular system to change from the normal state for the distribution constant μ and parameters a_1, a_2, \dots, a_e (the statistical-mechanical (S.M.) variables) to the normal state for values $\mu + \delta\mu, a_1 + \delta a_1, a_2 + \delta a_2, \dots, a_e + \delta a_e$ of the S.M. variables. The energy will alter to a value $E + \delta E$ where

$$\delta E = H(\mu + \delta\mu, a + \delta a) - H(\mu, a).$$

Of this change in the energy, a certain part is given by

$$\sum_{r=1}^c \left(\nu_r \frac{\partial \epsilon_r}{\partial a_1} \delta a_1 + \nu_r \frac{\partial \epsilon_r}{\partial a_2} \delta a_2 + \dots + \nu_r \frac{\partial \epsilon_r}{\partial a_e} \delta a_e \right)$$

We shall denote it by δE_1 , so that

$$\delta E_1 = \sum_{r=1}^c \sum_{s=1}^e \nu_r \frac{\partial \epsilon_r}{\partial a_s} \delta a_s \quad . \quad . \quad . \quad (6.2.1)$$

This part arises from the change in the parameters, but with the distribution still kept at the original normal state ($n_r = \nu_r$) and not altered to the new normal state ($n_r = \nu_r + \delta \nu_r$). The remainder of the energy $\delta E_2 (= \delta E - \delta E_1)$ is given by

$$\delta E_2 = \sum_{r=1}^c \sum_{s=1}^e \epsilon_r \frac{\partial \nu_r}{\partial a_s} \delta a_s + \sum_{r=1}^c \epsilon_r \frac{\partial \nu_r}{\partial \mu} \delta \mu \quad . \quad . \quad . \quad (6.2.2) *$$

The first part, δE_1 , does not arise from effective changes in the *co-ordinates and momenta* of the molecules; for the numerical distribution of phases among the cells is regarded as unaltered in estimating δE_1 . The part δE_2 does arise from the changes in cell-distribution occasioned by the changes in the parameters and μ . It is plausible to regard this second part as the analogue of the heat supplied to the system and the first part as the analogue of energy transferred to the system by purely mechanical means. We recall the fact that among the parameters are a group related to

* Remember that the ϵ_r do not depend on μ .

an external field of force which limits the volume of the molecular system ; any change in these involves alteration in the boundary and work of an " external pressure." Thus δE_1 may be regarded as the analogue of " external work " done *on* the system.

Quite apart from such interpretation, however, it can be deduced as a matter of mathematics only that, with δE_1 and δE_2 defined as in (6.1.1) and (6.1.2),

$$\mu \delta E_2 = \delta \{ \mu [H(\mu, a) - \Psi(\mu, a)] \} \quad (6.2.3)$$

We shall defer the actual mathematical steps for a moment so as not to interrupt the general line of thought. Suppose the molecular system to experience a *finite* change from a normal state (μ', a') to a normal state (μ'', a'') *passing through all the intermediate normal states* on its way (just as in thermodynamic reasoning a physical system is supposed to pass from state to state through intermediate states of thermodynamic equilibrium), then

$$\begin{aligned} \int_{s'}^{s''} \mu dE_2 &= \int_{s'}^{s''} d\{ \mu [H - \Psi] \} \\ &= \mu'' [H(\mu'', a'') - \Psi(\mu'', a'')] - \mu' [H(\mu', a') - \Psi(\mu', a')]. \end{aligned}$$

Thus the integral of μdE_2 from the state s' to state s'' *along a track of normal states* depends only on the initial and final states. The analogy with the entropy-theorem of thermodynamics is obvious. On interpreting δE_2 as heat supplied to the system, and $(k\mu)^{-1}$ as the temperature θ , we have

$$\int_{s'}^{s''} \frac{dE_2}{\theta} = \Phi(\mu'', a'') - \Phi(\mu', a')$$

where

$$\Phi(\mu, a) = k\mu [H(\mu, a) - \Psi(\mu, a)] \quad (6.2.4)$$

and is the analogue of the entropy-function of the thermodynamic state of the physical system.

To complete the analogy we have to discover the statistical-mechanical theorem corresponding to the increase of entropy which takes place when an *isolated* physical system passes in an irreversible manner from one state of equilibrium to another. Such an irreversible change takes place through intermediate states some of which at least are not states of

equilibrium. Hence in the statistical-mechanical analogue we must conceive of some way in which a molecular system in a normal state may pass to another normal state through intermediate states which are not all normal. This can easily be effected. In the thermodynamic processes we alter the thermodynamic variables from the values which hold for the first state to those which hold for the second in a short time. This ensures irreversibility of the path. The essence of reversibility is the infinitely slow change in the variables allowing the system to pass through intermediate states of equilibrium. Similarly we quickly change the S.M. variables from the values μ', a' for the first state to the values μ'', a'' for the second state. To carry through the reasoning we require to know another mathematical result, the proof of which we shall also defer for a moment; it is this:—

$$\Phi(\mu, a) = k(\log W_m - n \log n) \quad . \quad . \quad (6.2.5)$$

where W_m is the maximum value of the function $W(n_1, n_2, \dots, n_c)$ being equal in fact to $W(\nu_1, \nu_2, \dots, \nu_c)$.

Suppose then the molecular system is in the normal state characterised by $(\mu', a'_1, a'_2, \dots, a'_c)$; a sudden change is made in the S.M. variables to the values $\mu'', a''_1, a''_2, \dots, a''_c$.^{*} The distribution $\nu'_1, \nu'_2, \dots, \nu'_c$ is no longer the normal distribution for the new variables; the normal distribution is $\nu''_1, \nu''_2, \dots, \nu''_c$.

Hence

$$W(\nu'_1, \nu'_2, \dots, \nu'_c) < W(\nu''_1, \nu''_2, \dots, \nu''_c)$$

for the latter is the maximum value of the function $W(n_1, n_2, \dots, n_c)$ for the new parameters and distribution-constant. At the beginning of the change the system although in a normal state for the old S.M. variable is in an abnormal state for the new S.M. variables, and by our probability-postulate it will ultimately arrive at and keep very near to the normal state for these new values. It may experience all sorts of changes on the way; W may fluctuate about in the most fortuitous way (we cannot follow the individual history of

^{*} Remember that there is no change of energy. The system is to be isolated. Hence changing parameters will in general involve a change of μ also, so as to satisfy $H(\mu', a') = H(\mu'', a'')$.

each particle), but presently the system will reach the new normal state with the increased value of W . If W_m' is the value of W ($\nu_1', \nu_2', \dots, \nu_c'$) and W_m'' is the value of W ($\nu_1'', \nu_2'', \dots, \nu_c''$), W_m' was the maximum value for the S.M. variables in first state, just as W_m'' is for the second; and since $W_m' < W_m''$, therefore by (6.2.5)

$$\Phi(\mu', a') < \Phi(\mu'', a'').$$

Thus in the statistical-mechanical argument the function $\Phi(\mu, a)$ behaves in a manner similar to the mode of behaviour of entropy in Thermodynamics.

We have to fill in the missing mathematical steps leading to (6.2.3) and (6.2.5). They are three in number.

I.—Since any one of the equations (6.1.1) is an identity when the ν_r , λ and the ϵ_r are regarded as functions of μ and the a_s , the result of partial differentiation with respect to μ or any of the a_s still yields identities. Hence we have the c equations

$$\frac{\partial \log \nu_r}{\partial a_s} = \frac{\partial \lambda}{\partial a_s} - \mu \frac{\partial \epsilon_r}{\partial a_s}$$

for any given a_s .

This is the same as

$$\frac{\partial \nu_r}{\partial a_s} = \nu_r \frac{\partial \lambda}{\partial a_s} - \mu \nu_r \frac{\partial \epsilon_r}{\partial a_s}.$$

On adding the c equations we obtain

$$\frac{\partial n}{\partial a_s} = n \frac{\partial \lambda}{\partial a_s} - \mu \sum_{r=1}^c \nu_r \frac{\partial \epsilon_r}{\partial a_s}.$$

But, since n does not change, $\partial n / \partial a_s = 0$, and so

$$\sum_{r=1}^c \nu_r \frac{\partial \epsilon_r}{\partial a_s} = \frac{\partial \Psi(\mu, a)}{\partial a_s}.$$

Thus

$$\sum_{r=1}^c \sum_{s=1}^c \nu_r \frac{\partial \epsilon_r}{\partial a_s} \delta a_s = \sum_{s=1}^c \frac{\partial \Psi(\mu, a)}{\partial a_s} \delta a_s.$$

But

$$\delta \Psi(\mu, a) = \frac{\partial \Psi(\mu, a)}{\partial \mu} \delta \mu + \sum_{s=1}^c \frac{\partial \Psi(\mu, a)}{\partial a_s} \delta a_s.$$

Hence

$$\delta E_1 = \delta \Psi (\mu, a) - \frac{\partial \Psi (\mu, a)}{\partial \mu} \delta \mu.$$

As $\delta E_2 = \delta E - \delta E_1$ it follows that

$$\delta E_2 = \delta H (\mu, a) - \delta \Psi (\mu, a) + \frac{\partial \Psi (\mu, a)}{\partial \mu} \delta \mu \quad (6.2.6)$$

II.—Reverting to (6.1.1) once more, we obtain the equations

$$\frac{\partial \log \nu_r}{\partial \mu} = \frac{\partial \lambda}{\partial \mu} - \epsilon_r,$$

or

$$\frac{\partial \nu_r}{\partial \mu} = \nu_r \frac{\partial \lambda}{\partial \mu} - \nu_r \epsilon_r,$$

which on addition yield the result

$$n \frac{\partial \lambda}{\partial \mu} = E.$$

So that

$$\frac{\partial [\mu \Psi (\mu, a)]}{\partial \mu} = H (\mu, a),$$

or

$$\frac{\partial \Psi (\mu, a)}{\partial \mu} = \frac{H (\mu, a) - \Psi (\mu, a)}{\mu} \quad . \quad . \quad (6.2.7)$$

Combining (6.2.6) and (6.2.7), we have the result

$$\delta E_2 = \delta [H (\mu, a) - \Psi (\mu, a)] + \frac{H (\mu, a) - \Psi (\mu, a)}{\mu} \delta \mu$$

or

$$\mu \delta E_2 = \delta \left\{ \mu [H (\mu, a) - \Psi (\mu, a)] \right\},$$

which is equation (6.2.3).

III.—Lastly, on putting the values for ν_r in the expression for $\log W$, we obtain

$$\begin{aligned} \log W_m &= n \log n - \sum_{r=1}^c \nu_r (\lambda - \mu \epsilon_r) \\ &= n \log n - n\lambda + \mu E. \end{aligned}$$

So

$$\mu [H (\mu, a) - \Psi (\mu, a)] = \log W_m - n \log n,$$

and

$$\Phi(\mu, a) = k(\log W_m - n \log n),$$

which is equation (6.2.5).

The molecular models which we employ thus give us a somewhat broader view of the property which we call "entropy" than pure Thermodynamics. The function $W(n_1, n_2, \dots, n_c)$, is one which does not maintain a constant value in the actual history of a molecular system; there are continual fluctuations in its value going on as the numbers n_1, n_2, \dots, n_c change with the individual movements and encounters of the molecules. The probable amounts of these fluctuations we shall estimate later, but they are on the average small, although there is no dynamical impossibility in brief excursions to values very far removed from the normal ν . So if we adopt the terminology of Darwin and Fowler, and call

$$k\{\log W(n_1, n_2, \dots, n_c) - n \log n\},$$

the "kinetic entropy" of the system, we know that this kinetic entropy is fluctuating between its maximum value and values slightly below it, except for very occasional wider fluctuations to values well below. In thermodynamics, which is built on "macroscopic" observation, not "microscopic" analysis, we rest our reasoning on experimental results in which these fluctuations become "smoothed out," and an appearance of statical rest rather than of statistical equilibrium is presented, leading to the conception of a non-fluctuating thermodynamic entropy for whose value we naturally take the maximum value of the kinetic entropy. In thermodynamics, moreover, entropy is a property which can only be defined for states of equilibrium. In Statistical Mechanics, kinetic entropy is not so restricted to normal states alone.

To conclude this chapter we have to point out that the function $\Psi(\mu, a)$ is the analogue of the free-energy function (at constant volume) of a thermodynamic system. Thus (6.2.4) can be written

$$\Psi = H - \theta \Phi,$$

and, moreover,

$$\begin{aligned}\frac{\partial \Psi}{\partial \theta} &= \frac{\partial \Psi}{\partial \mu} \frac{d\mu}{d\theta} \\ &= \frac{\partial \Psi}{\partial \mu} \bigg/ \frac{d\theta}{d\mu} \\ &= -k\mu^2 \frac{\partial \Psi}{\partial \mu}\end{aligned}$$

$$\begin{aligned}\text{which, by (6.2.7)} \quad &= -k\mu (H - \Psi) \\ &= \Phi.\end{aligned}$$

These two results connecting $\Psi(\mu, a)$ with $H(\mu, a)$ and $\Phi(\mu, a)$, are obviously formally similar to the mathematical equations connecting the free-energy function with the energy and entropy functions in Thermodynamics.

CHAPTER VII

THE ENTROPY OF A PERFECT GAS

7.1 The Problem of the Magnitude of a Phase-Cell.—In Chapter IV. we carried through some mathematical operations which involved the substitution of integrations of continuous functions of phase for summations of a number of terms of a series. The nature of the problems which we were discussing at that point is such that no ambiguity results from this procedure. It is quite otherwise with the investigation on which we are now about to fasten attention. In the immediately preceding sections we have obtained an expression for the entropy of a monatomic gas ; it is

$$k (\log W_m - n \log n)$$

$$\text{or} \quad -k \sum_{r=1}^c \nu_r \log \nu_r.$$

Naturally we are concerned to discover the connection of this expression with the well-known thermodynamic expression for the entropy of a gas, *viz.*,

$$s_p \log \theta - R \log p + \text{constant}$$

where s_p is the heat-capacity at constant pressure. The two mathematical expressions do not bear a very obvious resemblance to one another ; yet the conversion of the former into an integral leads quite directly after a few steps to a demonstration of their essential agreement. But there is one step in the conversion which has been the origin of one of the most famous scientific discussions of the past two decades, and has led to results which are in some quarters regarded as one of the prime achievements of the quantum theory outside its triumphs in settling questions of atomic structure.

In Chapter IV. we replace n_r by a sextuple integral

$$\int \dots \int f(\xi, \eta, \zeta, x, y, z) d\sigma,$$

where $d\sigma$ is written as a symbol for the infinitesimal element of phase-extension

$$d\xi \, d\eta \, d\zeta \, dx \, dy \, dz,$$

and the integration is extended over limits determined by the r^{th} phase-cell. Now we clearly cannot replace $\log n_r$ by

$$\int \dots \log f \, d\sigma,$$

$$\text{nor } n_r \log n_r \text{ by } \int \dots f \log f \, d\sigma.$$

Strictly $n_r \log n_r$ is the product of $\int \dots \int f \, d\sigma$ and $\log \int \dots \int f \, d\sigma$, both integrations extending over a phase-cell. If we wish to replace $n_r \log n_r$ by an integral over the r^{th} phase-cell, and not by a product of an integral and its logarithm, we must begin by introducing a symbol for the magnitude of the cell; let it be g . Then n_r/g is the average value of the function f over the phase-cell; it is the average density of the representative points in the cell. It follows that there is an approximate equality between $\log (n_r/g)$ and the value of $\log f$ at any phase of the cell, and so there is an approximate equality between the integral

$$\int \dots \int f \log f \, d\sigma,$$

and the expression

$$n_r \log \left(\frac{n_r}{g} \right)$$

or

$$n_r \log n_r - n_r \log g.$$

It follows that there is an approximate equality between

$$\sum_{r=1}^c n_r \log n_r,$$

and the expression

$$\int \dots \int f \log f \, d\sigma + n \log g,$$

the integration being between the extreme limits of the phase-diagram. For the normal state we have seen in

Chapter IV. that the form of the function f (ignoring any external field of force) is

$$D \exp \{ -\alpha (\xi^2 + \eta^2 + \zeta^2) \}$$

where

$$\alpha = \frac{3n}{4\pi m E} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.1.1)$$

$$\text{and} \quad D = \frac{n}{v} \left(\frac{3n}{4\pi m E} \right)^{\frac{3}{2}} \quad . \quad . \quad . \quad . \quad (7.1.2)$$

and so there is an approximate equality between

$$\sum_{r=1}^c \nu_r \log \nu_r$$

and

$$D \int \dots \int \left[\exp \{ -\alpha (\xi^2 + \eta^2 + \zeta^2) \} \right] \\ \times \left[\log D - \alpha (\xi^2 + \eta^2 + \zeta^2) \right] d\sigma + n \log g. \quad . \quad (7.1.3)$$

the integration extending between the widest limits of the phase-diagram.

The quantity g is very vague at the moment. We only know two things about it. Although not a mathematical infinitesimal, it is "physically small" from the point of view of the experimentalist; yet it must be large enough to contain very many representative points in the region of the phase-diagram favoured by the points in the normal state. Further its physical dimensions in terms of the fundamental quantities length, time and mass are the same as the cube of the quantity "action," which is defined as the product of energy and time, and is a concept of great importance in the general mathematical formulation of classical dynamical principles; for the product of energy and time has clearly the same dimensions as the product of momentum and length. Nothing more can be elicited about g from classical sources.

It is more than twenty years since Planck made a very definite proposal about its magnitude. He suggested that there is a *precise definite* value for g which makes the equality mentioned above not merely approximate but *exact*. Natu-

rally such a statement could only be advanced with the support of some physical facts hitherto unnoticed. The facts which Planck appealed to were just those newly-observed phenomena which were at the time leading to the acceptance of a rather indefinite form of quantum hypothesis with its then revolutionary idea of a kind of atomicity in atomic occurrences previously unsuspected. There was also a new development in purely thermodynamic theory which was proving a fertile instrument of progress in the hands of Nernst and his pupils. Naturally we cannot enter into a discussion of these matters here, and must leave until later chapters some account of the repercussions on statistical mechanics of the quantum theory. But these remarks and the mathematical analysis in the next page or so will serve to prepare the reader for a fuller statement at a later stage. He is already probably aware that one fundamental feature of the quantum theory is the significance of a certain unit, or, if you like, "atom," of action known as "Planck's constant," and denoted by the symbol h . In terms of the erg-second as a working unit of action, the value of h has been determined in several ways to be 6.55×10^{-27} ; and to cut the matter short at the moment, the upshot of a great deal of discussion and experiment has been the suggestion that $g = h^3$, since, as pointed out above, g has the dimensions of action cubed. Without taking any other step for the present than that of using g to represent a precise physical magnitude, let us proceed.

7.2 The Entropy Constant.—By (7.1.3) the entropy of the gas becomes

$$kaD \int \dots \int (\xi^2 + \eta^2 + \zeta^2) \exp\{-a(\xi^2 + \eta^2 + \zeta^2)\} d\sigma \\ - kD \log D \int \dots \int \exp\{-a(\xi^2 + \eta^2 + \zeta^2)\} d\sigma - kn \log g$$

The first term is simply $2 kamE$, or, by (7.1.1), $3 nk/2$. The second term similarly reduces to $n k \log D$. Thus the entropy of the gas becomes

$$\frac{3}{2} nk - n k \log D - n k \log g.$$

On inserting the value of D from (7.1.2), and completing a few obvious steps, we arrive at

$$n k \left\{ \frac{3}{2} \log E + \log v - \frac{5}{2} \log n + \frac{3}{2} \left(1 + \log \frac{4 \pi m}{3} \right) - \log g \right\}$$

Since $E = 3 n k \theta / 2$, we easily obtain for the entropy of a monatomic gas containing n molecules the expression

$$n k \left\{ \frac{3}{2} \log \theta + \log v - \log n + \log \frac{(2 \pi m k)^3}{g} + \frac{3}{2} \right\},$$

which, on changing from the variable v to p by means of

$$p v = R \theta = n k \theta,$$

or $\log v = \log \theta - \log p + \log n + \log k$
becomes

$$R \left\{ \frac{5}{2} \log \theta - \log p + \log \frac{(2 \pi m k)^3 k}{g} + \frac{3}{2} \right\} \quad (7.2.1)$$

The formal similarity of (7.2.1) with the thermodynamic expression for the entropy of a gas is apparent. In view of Planck's hypothesis concerning the definiteness of the magnitude of g , it goes further than pure thermodynamics, for it suggests a precise value for the undetermined constant of integration which enters in the thermodynamic analysis. Now this is tantamount to asserting that a quantity of gas has at a definite pressure and temperature an *absolute* entropy, a position quite untenable in the classical thermodynamics of the nineteenth century in which only differences of entropy between two assigned states were considered. But, as mentioned already, Nernst's heat theorem, and the work carried out in his laboratory on measuring the affinities of chemical reactions and the specific heats of gases and condensed materials at low temperatures, had in the early years of this century carried physical chemists at all events well away from the vagueness of the older position, even before the full blast of the quantum theory had played havoc with classical methods and conceptions. We cannot pursue this particular matter further at the moment. The main problem of this chapter has been to show the essential agreement between two formally very different expressions, and that has been achieved. We must pass on to further developments of statistical theory along classical lines.

CHAPTER VIII

THE STATISTICAL THEORY OF CHEMICAL EQUILIBRIUM IN A GAS REACTION

8.1 Reactions Equivalent to a Simple Dissociation.—Let us consider a system in which there exist atoms of two different types and diatomic molecules, each containing one atom of each type. The phase diagram represents the Cartesian co-ordinates of the centres of gravity of the dissociated atoms and of the molecules and the corresponding momenta; it is, of course, six dimensional. Let there be present in all α atoms of one type and β of the other; so that if the *dissociated* atoms at any moment are a and b of each kind respectively, then the number of molecules at that moment is l , where

$$\begin{aligned} a + l &= \alpha \\ b + l &= \beta \end{aligned} \quad . \quad . \quad . \quad . \quad . \quad (8.1.1)$$

It is assumed that the formation of a molecule or its dissociation is accompanied by the liberation or absorption of a definite amount of energy. Thus, if there is no external field of force, the energies of the atoms and the molecules in a certain phase are given by

$$\begin{aligned} \epsilon_a &= \frac{\xi^2 + \eta^2 + \zeta^2}{2 m_a} \\ \epsilon_b &= \frac{\xi^2 + \eta^2 + \zeta^2}{2 m_b} \quad . \quad . \quad . \quad . \quad (8.1.2) \\ \epsilon_r &= \frac{\xi^2 + \eta^2 + \zeta^2}{2 (m_a + m_b)} - w \end{aligned}$$

where w is a definite energy of dissociation and is regarded as positive if energy is absorbed in the dissociation of a molecule.

In counting complexions we have to analyse the situation

more exhaustively than in earlier chapters. Let us consider the state in which

a_1 atoms of first type, b_1 atoms of second type,
 l_1 molecules are in cell 1.

a_2 atoms of first type, b_2 atoms of second type,
 l_2 molecules are in cell 2.

.

a_c atoms of first type, b_c atoms of second type,
 l_c molecules are in cell c .

The first step begins by supposing that we have a *particular* atoms of the first type, b *particular* atoms of the second type, and l *particular* molecules to deal with; a , of course, being Σa_r , b being Σb_r , and l being Σl_r . There are, of course,

$$\frac{a!}{a_1! a_2! \dots a_c!}$$

ways of distributing the first type atoms in the manner indicated.

$$\frac{b!}{b_1! b_2! \dots b_c!}$$

ways of distributing the second-type atoms; and

$$\frac{l!}{l_1! l_2! \dots l_c!}$$

ways of distributing the molecules. The product of these three expressions is then the number of different ways of producing the state indicated *with the particular atoms and molecules chosen*. But the italicised phrase shows us that we have by no means obtained all the complexions embraced within the state indicated.

We have, in fact, to bear in mind that we can select a atoms from the given total number, a , of first-type atoms in

$$\frac{a!}{a! (a - a)!} \text{ or } \frac{a!}{a! l!}$$

ways, and b atoms from the β atoms of the second type in

$$\frac{\beta!}{b! l!}$$

ways. Hence the previous product must again be multiplied by these two factors since a change of the individuality of a single atom in a cell yields a different complexion. Nor is this all. Having selected the dissociated atoms of each type, we have by no means settled the individuality of the molecules although we have, by reason of the selection mentioned, chosen the $2l$ atoms out of which they are to be constituted. Let us consider a definite complexion obtained as indicated. Without altering the individualities or numbers of the atoms in the cells, and without altering the numbers of the molecules in the cells, we can obtain $l!$ complexions from this one complexion by permuting the atoms in the molecules. It is just as if we had dumb-bells each made with a red and a black ball arranged in a particular scheme. Imagine the red balls to be removable; there are $l!$ different ways of arranging them in the l places of the scheme and attaching them to the fixed black balls. Thus to obtain the total number of complexions consistent with the state described, we have to multiply the product of the previous five expressions by $l!$. The final result is

$$\frac{\alpha! \beta!}{a_1! a_2! \dots a_c! b_1! b_2! \dots b_c! l_1! l_2! \dots l_c!} \quad (8.1.3)$$

The calculation of the most probable state proceeds as before by taking the logarithm of this expression and varying it under the assigned conditions of number and energy. Using the Stirling approximation, we obtain the following variational equations for the state of maximum probability

$$\Sigma \log a_r \delta a_r + \Sigma \log b_r \delta b_r + \Sigma \log l_r \delta l_r = 0$$

$$\Sigma \delta a_r + \Sigma \delta l_r = 0$$

$$\Sigma \delta b_r + \Sigma \delta l_r = 0$$

$$\Sigma \epsilon_{ar} \delta a_r + \Sigma \epsilon_{br} \delta b_r + \Sigma \epsilon_{lr} \delta l_r = 0$$

These, by the method of undetermined multipliers, give us 3 c equations

$$\begin{aligned}\log a_r + \lambda_a + \mu \epsilon_{ar} &= 0 \\ \log b_r + \lambda_b + \mu \epsilon_{br} &= 0 \quad . \quad . \quad . \quad (8.1.4) \\ \log l_r + \lambda_a + \lambda_b + \mu \epsilon_{lr} &= 0\end{aligned}$$

These equations combined with

$$\begin{aligned}\Sigma a_r + \Sigma l_r &= a \\ \Sigma b_r + \Sigma l_r &= \beta \\ \Sigma a_r \epsilon_{ar} + \Sigma b_r \epsilon_{br} + \Sigma l_r \epsilon_{lr} &= E\end{aligned}$$

are sufficient to determine the $3c + 3$ quantities, λ_a , λ_b , μ and the a_r , b_r , l_r in terms of E , n and the parameters. The usual feature of a common distribution constant appears once more and in the normal state the numbers are

$$\begin{aligned}a_r &= A \exp(-\mu \epsilon_{ar}) \\ b_r &= B \exp(-\mu \epsilon_{br}) \quad . \quad . \quad . \quad (8.1.5) \\ l_r &= A B \exp(-\mu \epsilon_{lr}) \\ A &= \exp(-\lambda_a) \\ B &= \exp(-\lambda_b)\end{aligned}$$

where

The well-known mass-law follows at once from this. For the total number of atoms of the first type in the normal state is given by an integral (after the manner of Chapter IV.) such as

$$\begin{aligned}a &= \frac{A}{g} \int \dots \dots \int \exp(-\mu \epsilon_a) d\sigma \\ &= \frac{A}{g} \left(\frac{2 m_a \pi}{\mu} \right)^{\frac{3}{2}} \\ b &= \frac{B}{g} \left(\frac{2 m_b \pi}{\mu} \right)^{\frac{3}{2}} \\ l &= \frac{AB}{g} \left(\frac{2 (m_a + m_b) \pi}{\mu} \right)^{\frac{3}{2}} e^{\mu w}.\end{aligned}$$

Thus, since the concentrations are proportional to the numbers, we have the usual law

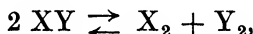
$$\frac{C_a C_b}{C_l} = K$$

where K is the equilibrium-constant depending on the temperature and the energy. Further, since $K \propto e^{-\mu w}$

$$\begin{aligned}\frac{d \log K}{d\theta} &= \frac{w}{k\theta^2} \quad . \quad . \quad . \quad (8.1.6) \\ &= \frac{Q}{R\theta^2},\end{aligned}$$

where Q is the heat of dissociation of a gram-molecule of the molecular compound.

8.2 Reactions in which the Number of Molecules is Unchanged.—Turning to a reaction in which two molecules of the type XY yield one molecule of the type X_2 and one of the type Y_2 symbolised by



we have in a particular state l molecules of XY , a of X_2 and b of Y_2 , so that if α is the total (and given) number of atoms X , and β the total number of atoms Y present, then

$$\begin{aligned}2a + l &= \alpha \\ 2b + l &= \beta\end{aligned} \quad . \quad . \quad . \quad (8.2.1)$$

Each molecule is characterised by a definite amount of internal potential energy over and above its kinetic energy as a whole,* so that

$$\begin{aligned}\epsilon_a &= \frac{\xi^2 + \eta^2 + \zeta^2}{4 m_a} + w_a \\ \epsilon_b &= \frac{\xi^2 + \eta^2 + \zeta^2}{4 m_b} + w_b \quad . \quad . \quad . \quad (8.2.2) \\ \epsilon_l &= \frac{\xi^2 + \eta^2 + \zeta^2}{2 (m_a + m_b)} + w_l\end{aligned}$$

where w_a , w_b , w_l are definite amounts of energy, positive or negative.

The counting of complexions proceeds on much the same lines as before. Considering a state as defined in section

* We are excluding rotational energy. This could be treated by fresh co-ordinates and extending the dimensionality of the phase-diagram. It would complicate the mathematics without adding anything vital to the discussion at this point.

(8.1) we have, so long as we particularise the molecules, to obtain the number of complexions by multiplying

$$\frac{a!}{a_1! a_2! \dots a_c!} \cdot \frac{b!}{b_1! b_2! \dots b_c!} \cdot \frac{l!}{l_1! l_2! \dots l_c!}$$

But for any complexion we can select the $2a$ atoms in the X_2 -molecules in

$$\frac{a!}{2a! (a - 2a!)} \quad \text{or} \quad \frac{a!}{2a! l!}$$

ways out of the a X-atoms; and out of the β Y-atoms we select the $2b$ Y_2 -molecules in

$$\frac{\beta!}{2b! l!}$$

ways. As before, this does not exhaust the possibilities. In any choice we are left with l particular X-atoms and l particular Y-atoms to make the l XY-molecules; but out of any complexion with particular XY-molecules we make $l!$ new complexions by keeping the X-atoms of these molecules fixed, as it were, in the design and permuting the Y-atoms in all possible ways; for thus we form new molecules with the same atoms as before. We must be careful in applying a similar process to the X_2 -molecules. Out of any complexion with a particular X_2 -molecules, it would look as if we could make $2a!$ new complexions by permuting the $2a$ atoms all possible ways in the design; but this gives us too large a result; for many of these would only be replicas of other complexions (in the same state) made with the same a X_2 -molecules. Any permutation which did not destroy the companionship of the pairs of atoms would do this, and this fact shows us that the complete permutations suggested would reproduce definite complexions over and over again as many times as there are permutations of the a molecules (each regarded as a unity) in the scheme. But this number of times is $a!$, and so out of the particular complexion with a particular X_2 -molecules, we can only produce $2a!/a!$ new complexions by permutation of the atoms. A similar remark applies to the Y_2 -molecules. Thus the product of the five expressions quoted above must be multiplied by

$l!$, $2a!/a!$ and $2b!/b!$ to obtain the number of complexions possible for the state mentioned. It is

$$\frac{\alpha! \beta!}{a_1! a_2! \dots a_c! b_1! b_2! \dots b_c! l_1! l_2! \dots l_c!}$$

as before. The normal state is obtained by the variational equations of the type

$$\Sigma \log a_r \delta a_r + \Sigma \log b_r \delta b_r + \Sigma \log l_r \delta l_r = 0$$

$$2 \Sigma \delta a_r + \Sigma \delta l_r = 0$$

$$2 \Sigma \delta b_r + \Sigma \delta l_r = 0$$

$$\Sigma \epsilon_{ar} \delta a_r + \Sigma \epsilon_{br} \delta b_r + \Sigma \epsilon_{lr} \delta l_r = 0,$$

leading to 3 c equations such as

$$\log a_r + 2 \lambda_a + \mu \epsilon_{ar} = 0$$

$$\log b_r + 2 \lambda_b + \mu \epsilon_{br} = 0$$

$$\log l_r + (\lambda_a + \lambda_b) + \mu \epsilon_{lr} = 0$$

and three further equations depending on total numbers and energy. Thus in the normal state

$$\begin{aligned} a_r &= A^2 \exp(-\mu \epsilon_{ar}) \\ b_r &= B^2 \exp(-\mu \epsilon_{br}) \\ l_r &= AB \exp(-\mu \epsilon_{lr}) \end{aligned} \quad . \quad . \quad (8.2.3)$$

where

$$A = \exp(-\lambda_a)$$

$$B = \exp(-\lambda_b)$$

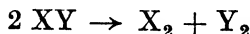
This result, combined with (8.2.2), leads directly to the result that

$$\frac{C_a C_b}{C_l^2} = K$$

where K is the equilibrium constant and is proportional to

$$\exp\{-\mu (w_a + w_b - 2 w_l)\}$$

The expression $w_a + w_b - 2 w_l$ is the energy absorbed in the reaction



and yielded in the reverse reaction, so as before

$$\frac{d \log K}{d\theta} = \frac{Q}{R\theta^2}$$

where Q is the heat of reaction at temperature θ .

8.3 Generalisation for Any Type of Reaction.—The method of procedure for any type of gas reaction is now fairly obvious.

Let there be in all α atoms of type X, β atoms of type Y, γ atoms of type Z, and so on. In the reaction there occur molecules containing x_1 of the X-atoms, y_1 of the Y-atoms, z_1 of the Z-atoms, etc., x_1, y_1, z_1 , etc., being positive integers; these we shall call L_1 -molecules. There will also be L_2 -molecules, containing x_2 of the X-atoms, y_2 of the Y-atoms, z_2 of the Z-atoms, etc., and so on. The reaction follows some stoichiometric equation, such as

$$\nu_1 L_1 + \nu_2 L_2 + \nu_3 L_3 + \dots = 0$$

where $\nu_1, \nu_2, \nu_3, \dots$ are integers, some positive, some negative. This being so, the following equations must be true

$$\begin{aligned} \nu_1 x_1 + \nu_2 x_2 + \nu_3 x_3 + \dots &= 0 \\ \nu_1 y_1 + \nu_2 y_2 + \nu_3 y_3 + \dots &= 0 \quad (8.3.1) \\ \nu_1 z_1 + \nu_2 z_2 + \nu_3 z_3 + \dots &= 0 \\ \vdots & \\ \vdots & \end{aligned}$$

The energies of the molecules in a given phase of position and translational momentum are for an L_1 -molecule

$$\epsilon_1 = \frac{\xi^2 + \eta^2 + \zeta^2}{2 m_1} + w_1 \quad . \quad . \quad (8.3.2)$$

for an L_2 -molecule

$$\epsilon_2 = \frac{\xi^2 + \eta^2 + \zeta^2}{2 m_2} + w_2$$

and so on, where w_1, w_2, \dots are definite internal energies, and m_1, m_2, \dots are masses of the respective molecules. The heat of reaction during the reaction of $\nu_1 L_1$ -molecules, $\nu_2 L_2$ -molecules, etc., is

$$\nu_1 w_1 + \nu_2 w_2 + \nu_3 w_3 + \dots \quad . \quad (8.3.3)$$

If now in any state there are present $l_1 L_1$ -molecules, $l_2 L_2$ -molecules, etc., then

$$\begin{aligned} x_1 l_1 + x_2 l_2 + x_3 l_3 + \dots &= \alpha \\ y_1 l_1 + y_2 l_2 + y_3 l_3 + \dots &= \beta \\ z_1 l_1 + z_2 l_2 + z_3 l_3 + \dots &= \gamma \end{aligned} \quad (8.3.4)$$

where M_1, M_2, \dots are numerical multipliers arising in the integrations. Owing to equations (8.3.1) it follows that

$$\begin{aligned} C_1^{\nu_1} C_2^{\nu_2} \dots &= M \exp \{ -\mu (\nu_1 w_1 + \nu_2 w_2 + \dots) \} \\ &= M \exp \left(-\frac{Q}{R\theta} \right), \end{aligned}$$

where M is equal to $M_1^{\nu_1} M_2^{\nu_2} \dots$.

and Q is the heat of reaction per gram molecule of reactants or resultants. Thus the equilibrium constant makes its appearance again as a quantity proportional to $\exp (-Q/R\theta)$ leading to

$$\frac{d \log K}{d\theta} = \frac{Q}{R\theta^2}.$$

CHAPTER IX

INTERMOLECULAR FORCES

9.1 The Effect of the Finite Sizes of Molecules.—In deriving the formula for the pressure of a gas in section (4.2) it was implicitly assumed that we were dealing with a swarm of point-particles. But the impossibility of crushing a body of liquid or solid into an infinitesimal volume is simple and direct evidence that whatever be the structure of molecules, they have finite size in the sense that the centres of two molecules cannot be forced nearer to one another than a certain definite distance, minute though it be. Contrasting two molecular systems, therefore, each one containing the same number of molecules in the same volume, but one being constituted of larger molecules than the other, it will be seen that the mean free path between collisions will be a trifle shorter in the first case than in the second. This will have the effect of slightly increasing the rate of transfer of molecules across an element of surface, thus producing at the same temperature, *i.e.*, at the same mean velocity, a somewhat enhanced rate of transference of momentum. The effect will be all the greater the larger the molecular size in comparison with mean free path, *i.e.*, the larger the concentration. We may, therefore, infer on general grounds that the pressure of a gas whose concentration is ν molecules per unit volume is given more accurately than before by some formula, such as

$$p = \nu \psi(\nu) k\theta,$$

where $\psi(\nu)$ is a function which approaches unity as ν approaches zero, and increases in value as ν increases. Expanding $\psi(\nu)$ as a series in ascending powers of ν , we can as a first approximation retain the first power of ν only and write

$$p = \nu (1 + \beta \nu) k\theta \quad . \quad . \quad . \quad (9.1.1)$$

as a somewhat amended form of the simple Boyle's law. From the reasoning employed, it will be realised that as between different gases, the constant β will be larger for larger molecules. We have in the reasoning implicitly idealised a collision as an instantaneous phenomenon. It is scarcely probable that the actual occurrence is dynamically so simple; still it is evident from the cohesion of solid and liquid matter and the broad facts of their compressibilities, that the repulsive forces called into play at the close encounter of two molecules disappears at a very small distance apart, and so the conversion of kinetic energy into potential energy during the encounter occupies a very brief time as compared with the mean interval between collisions. It is this fact concerning the intermolecular *repulsive* forces exerted at very near approach which allows us to dispose of them in the somewhat cavalier manner employed above.

9.2 Intermolecular Attraction.—The elementary application of the conception of molecular attraction to the explanation of latent heat of vaporisation of a liquid is no doubt known to the reader. In the interior of the fluid a molecule does not experience a constant force in any definite direction, as it is surrounded by molecules whose resultant pull on it will be on the average zero. Only in the molecular layer at the surface whose thickness is equal to the radius of molecular attraction (beyond which the force becomes negligible) will there be a resultant pull normally inwards. This can be regarded as equivalent to removing the molecular attraction and replacing it by an increased external pressure. The amount of this increase is not difficult to estimate. Let $f(r)$ represent the magnitude of the force between two molecules separated by a distance r . Consider a particular molecule, A, and the molecules surrounding it in a spherical shell between spheres of radii r and $r + \delta r$. Suppose the fluid to expand uniformly by a small amount so that there is a *linear* coefficient of extension of value ϵ ; as the mutual potential energy of two molecules will increase by the amount $f(r) \epsilon r$, it follows that the increase in the mutual potential energy of A and its neighbours in the shell will increase by

$$\epsilon r f(r) \nu 4 \pi r^2 \delta r.$$

Hence the increase in the mutual potential energy of A and all its neighbours is given by the integral

$$4 \pi \epsilon \nu \int_{\sigma}^{\infty} r^3 f(r) dr,$$

where σ is the nearest distance of approach of molecular centres. The increase in the whole potential energy of attraction of the molecules will be obtained by summing this for all the molecules and taking half the sum. (Otherwise the mutual energy of any pair of molecules would be counted twice.) The result is

$$2 \pi \epsilon n \nu \int_{\sigma}^{\infty} r^3 f(r) dr,$$

where n is the total number of molecules, so that $\nu = n/v$. But if an increase of volume δv accompanies the linear extension ϵ , then $\epsilon = \frac{1}{3} \delta v/v$, and so the result for the increase in potential energy is

$$\alpha \nu^2 \delta v,$$

where

$$\alpha = \frac{2 \pi}{3} \int_{\sigma}^{\infty} r^3 f(r) dr \quad . \quad . \quad . \quad (9.2.1)$$

If the work thus done in the expansion had been performed against an external pressure $\hat{\omega}$, instead of against molecular attraction, its value would have been to $\hat{\omega} \delta v$. Thus the change of momentum produced in the molecules by the cohesion exerted in the molecular layer is the same as that produced by an external pressure of amount $\alpha \nu^2$. This correction shows that the internal pressure, *i.e.*, the rate of transference of normal momentum across unit area in the interior of the fluid, is $p + \alpha \nu^2$ and not p . So, recalling the correction made in the previous section, we have

$$p + \alpha \nu^2 = \nu (1 + \beta \nu) k \theta \quad . \quad . \quad (9.2.2)$$

If we write $a = \alpha n^2$ and $b = \beta n$, we obtain as a better approximation to the equation of state than Boyle's law the following result

$$p + \frac{a}{v^2} = \frac{n k \theta}{v} \left(1 + \frac{b}{v} \right),$$

or putting $(1 + b/v)^{-1}$ approximately equal to $1 - b/v$

$$\left(p + \frac{a}{v^2}\right) (v - b) = R\theta \quad . \quad . \quad (9.2.3)$$

This is Van der Waal's famous equation, and of the various interesting conclusions to be drawn from it the reader can inform himself in text-books of physics or physical chemistry. We are here concerned with the effect produced on our statistical methods by the introduction of intermolecular force into the arguments, and we shall therefore concentrate on one result which follows from a study of the relation (9.2.3).

It is well known that if isothermal curves are drawn, using Van der Waal's equation, these curves show a characteristic feature when the temperature is low enough. Traveling along such an isothermal in the sense of increasing volume, the pressure diminishes to a minimum, then increases for a space, reaches a maximum value, and once more proceeds to diminish indefinitely. There are, in fact, two values of v where dp/dv is zero, and between them dp/dv is positive. Within this region of pressure there are, in fact, three values of v mathematically possible for each value of p (θ , of course, being given).* The one which lies on the part where dp/dv is positive is considered to be so physically unstable as to escape observation by reason of its transience if it were produced. Of the other two, one is considered to correspond to a vapour phase which may be in an absolutely stable unsaturated or saturated state, or in a less stable condition of supersaturation; the remaining value of v is associated with the liquid state, which in its turn may be in a relatively unstable superheated condition, or quite stable below its boiling point at the pressure. This interpretation, of course, implies that the temperature below which the particular form of the isothermals manifests itself is the critical temperature of the substance. In this way is the

* Since (9.2.3) is for given p and θ a cubic equation in v , there are, of course, three values of v possible for any value of p , whether within the range specified or no. But, of course, two of these may be imaginary, or if all are real, they will, if not in the range, lie on those parts of the curve (which, be it noted, has really two branches, one not being usually shown in the books) for which $v < b$ with which we are not physically concerned.

equation (9.2.3) linked up with the hypothesis that there is a continuity between the liquid and gaseous states of aggregation through intermediate *homogeneous* states which, however, although physically conceivable, could only have a very transient existence if actually produced. Before passing on to consider this fact from the point of view of the statistical methods employed in previous chapters, we may realise its possibility in a general way, apart from special analysis, as follows. The internal pressure, $R\theta/(v - b)$, is reduced by the cohesion, a/v^2 , in the surface-layer to the value, p , of the pressure actually observed. An increase in volume implies a diminished density, and therefore a decrease in the *internal* pressure, *i.e.*, a smaller rush of molecules across the *inner* surface of the molecular layer. But the diminished density also produces a diminished cohesion, and therefore less hindrance to these molecules in escaping across the outer surface of the layer, so that the net result might be actually a greater external pressure. Students, through a failure to grasp the real meaning of the symbol p , sometimes fall into the error of imagining that a homogeneous state of aggregation in which p increases with v , is physically *impossible*, "because," as they say, "it is impossible for the pressure to increase if the volume increases," thereby betraying the fact that they think that the symbol p refers to the internal pressure, concerning which the statement is true enough. The very great instability of such a state (not its impossibility in an absolute sense) can, however, be realised by conceiving it to exist and then considering what would happen if by reason of the molecular motion a small fluctuation began in the density of a small portion of it. In the ordinary way, if a small portion of a fluid expands, there is a reduced outrush of molecules from its original volume. The surrounding fluid is pouring in molecules at the normal rate, with the result that further fluctuation in this direction is checked, and a similar conclusion follows for a fluctuation involving transient increase of density. But in the state of aggregation imagined, this would not take place; the outrush is accompanied by a reduction in cohesion of such magnitude that the fluctuation

is not checked, but actually assisted to greater intensity, as the increasing outrush overwhelms the normal stream of molecules inwards. Thus would be set up an expansion of the original fluctuating element to a less dense and more stable state. Similarly an original fluctuation in some element, beginning with an increase of density, instead of being checked by an enhanced outflow of molecules from it, would be assisted on account of a too great increase in cohesion, and a consequent inhibition of the balancing outward stream, so that the normal inward stream from without would force molecules into the element and so produce a stable condensed phase therein. In some such way we can visualise the separation of the unstable phase into droplets of liquid and a saturated vapour phase.

9.3 The Probability of a Macroscopic State when Intermolecular Action is Involved.—The change introduced into the analysis of Chapter III. by the assumption of inter-molecular force is produced by the fact that the energy of a state specified by the numbers n_1, n_2, \dots, n_c of representative points in the phase-cells is no longer a *linear* function of those numbers, as was the case when we wrote E equal to $\sum \epsilon_r n_r$, the ϵ_r being functions of the parameters of the system. If we write a general function $f(n_1, n_2, \dots, n_c, a_1, a_2, \dots, a_e)$, or briefly $f(n, a)$ for the energy of the state, the variational equation (3.2.10) in section (3.2) must be replaced by

$$\sum \left(\log n_r + \lambda + \mu \frac{\partial f(n, a)}{\partial n_r} \right) \delta n_r = 0$$

leading to the result that we must determine the values of the n_r in the most probable state as well as the functions λ, μ in terms of n, E , and the parameters by means of the $c + 2$ equations

$$\begin{aligned} \log n_r + \lambda + \mu \frac{\partial f(n, a)}{\partial n_r} &= 0 \\ \sum n_r &= n \\ f(n, a) &= E \end{aligned}$$

As regards the function, $f(n, a)$, it will, apart from the linear terms in n_r (which involve kinetic energy and potential

energy arising from external bodies), depend on the quantities $\Sigma (n_r)_s$, this summation referring to the sum of the numbers n_r over those phase-cells which have one space-element in common. If the c phase-cells are constituted by associating each one of α elements of volume with each one of β elements of extension-in-momentum (c being therefore equal to $\alpha\beta$), then this summation is over the β phase-cells which have the s^{th} element of volume in common. Calling the sum N_s , we have

$$f(n, a) = \sum_{r=1}^c \epsilon_r n_r + \psi(N_1, N_2, \dots, N_\alpha, a_1, a_2, \dots, a_\epsilon),$$

ϵ_r being the sum of the kinetic and external potential energies in the r^{th} phase-cell. Hence

$$\begin{aligned} \frac{\partial f(n, a)}{\partial n_r} &= \epsilon_r + \frac{\partial \psi(N, a)}{\partial N_s} \frac{\partial N_s}{\partial n_r} \\ &= \epsilon_r + \frac{\partial \psi(N, a)}{\partial N_s} \\ &= \epsilon_r + \chi_s(N_1, N_2, \dots, N_\alpha). \end{aligned}$$

Here $\chi_s(N_1, N_2, \dots, N_\alpha)$ can be regarded as the increase in *mutual* potential energy produced by introducing one more molecule into the element of volume which is a constituent part of the r^{th} phase-cell. If we assume that the phase-cells are constructed in such manner that their constituent volume elements are considerably larger than the sphere of molecular interaction (which from what we know of the range of molecular forces is not at variance with the assumption of the *physical* smallness of those elements), we can take $\chi_s(N_1, N_2, \dots, N_\alpha)$ to be the mutual potential energy of one molecule with respect to all the rest in the s^{th} volume-element. It will, therefore, be a function of the concentration of the molecules in this element which we shall denote by ν_s ; so we write, instead of $\chi_s(N_1, N_2, \dots, N_\alpha)$, the functional form $\phi(\nu_s)$ of the one variable ν_s . If we could assume some simple law of force for the attractions, and if we could assume this law to hold down to any distance apart (virtually assuming the molecules to be point-centres of force), $\phi(\nu_s)$ would have the form $-a\nu_s$, a being a positive constant, and

the minus sign being due to the fact that for attractive forces potential energy decreases with decreasing separation of molecules and increasing concentration. But, of course, this overlooks the occurrence of intermolecular repulsions at close encounter. The fact that there is a finite limit to the value of ν under the greatest pressures conceivable, requires us to assume that although $\phi(\nu)$ may very well behave as $-a\nu$ for relatively small values of ν , yet for values approaching some maximum limit ν_0 , $\phi(\nu)$ must begin to increase in value not only up to zero once more, but actually to positive infinity if we are to regard concentrations beyond ν_0 as physically impossible. This is in fact the counterpart of the infinite value required for the pressure p in Van der Waal's equation to reduce v to the value b .

From these equations we now find for the number of molecules with representative points in the r^{th} phase-cell, in the most probable state the value

$$C \exp \{ -\mu [\epsilon_r + \phi(\nu_s)] \}$$

This, by summation over the β elements of extension-in-momentum, which linked up with the s^{th} element of volume yield β phase-cells, gives N_s as

$$C e^{-\mu\phi(\nu_s)} \sum_{r=1}^{\beta} e^{-\mu\epsilon_r} \quad . \quad . \quad . \quad . \quad (9.3.1)$$

N_s , if divided by the magnitude of the element of volume, gives ν_s , and since the summation can be as usual replaced by an integration over all values of momentum, we obtain finally the result

$$\begin{aligned} \nu_s &= D e^{-\mu\phi(\nu_s)} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\mu\epsilon_r} d\xi d\eta d\zeta \\ &= D \left(\frac{\mu}{2\pi m} \right)^{\frac{3}{2}} e^{-\mu\phi(\nu_s)} \quad . \quad . \quad . \quad (9.3.2) \end{aligned}$$

where D is a constant. We are disregarding any external field of force.

From (9.3.1) it follows just as before that $3/(2\mu)$ is the average kinetic energy of a molecule, in any element of volume, for the factor $e^{-\mu\phi(\nu_s)}$, being the same for all phase-

cells associated with that element of volume, does not invalidate any of the steps occurring in the calculation. Thus internal potential energy does not interfere any more than external with the validity of the law of energy-partition.

The result (9.3.2) shows that the most probable state is consistent with a uniform spatial density given by any root of the equation in

$$\nu = A \mu^{\frac{3}{2}} e^{-\mu\phi(\nu)} \quad . \quad . \quad . \quad . \quad (9.3.3)$$

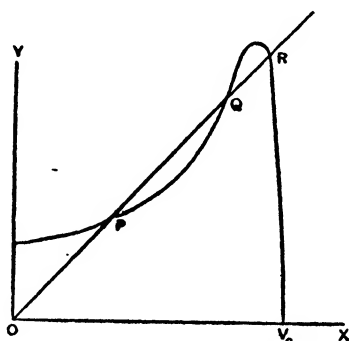
where A is a constant.

The easiest way to see how many roots are involved is to plot two graphs

$$y = \frac{x}{A \mu^{\frac{3}{2}}} \quad . \quad . \quad . \quad . \quad (9.3.4)$$

$$y = e^{-\mu\phi(x)} \quad . \quad . \quad . \quad . \quad (9.3.5)$$

the co-ordinate x representing the concentration ν . The roots of (9.3.3) are the abscissæ of the points of intersection of the graphs (9.3.4) and (9.3.5). Now if, as suggested by the neglect of forces of repulsion, $\phi(x)$ were taken to be $-ax$, there would either be two roots or none, according as the straight line $y = x/A\mu^{\frac{3}{2}}$, cut or did not cut the exponential curve, $y = e^{\mu ax}$. But if we take account of the finite size of the molecules, $-\phi(x)$, although increasing in proportion to x at first, will, as x gets very near to ν_0 in value, pass through a maximum and decrease through zero to minus infinity at $x = \nu_0$. Hence the curve, $y = e^{-\mu\phi(x)}$, will at a certain point in its exponential ascent abruptly turn down and y will decrease to zero at $x = \nu_0$.



The curve $y = e^{-\mu\phi(x)}$

We thus see the possibility of the straight line (9.3.4) cutting the curve (9.3.5) in *three* points. If, however, μ is reduced in value, *i.e.*, the temperature raised, the slope of the line will be increased, and the peak of the curve will not be so high, and so the line would only cut the curve in one point corresponding to a relatively small value of ν . If on the other hand μ is increased, the line will fall low, the curve will reach high; once more there will be only one point of intersection, this time, however, yielding a concentration close to ν_0 . We thus reproduce once more the result usually derived from Van der Waal's equation. The author has not met elsewhere this method of presenting the matter, but thinks it is perhaps worth while to outline it here, as it links up the result with the usual statistical method of estimating probabilities by counting complexions consistent with the energy conditions. However, in order to bring out the great instability of the state indicated by the point Q, we must appeal to a very ingenious piece of analysis first given by Smoluchowski in 1904. It arises in connection with the mathematical discussion of fluctuations in density of a molecular system. This will be dealt with in the next chapter.

CHAPTER X

FLUCTUATIONS OF DENSITY IN A MOLECULAR SYSTEM

10.1 The Probability of the Occurrence of a Prescribed Number of Molecules in an Element of Volume.—Reverting to the fundamental formula of the theory, we find that when uniform concentration of molecules in a definite volume is the most probable state (there being no *external* field of force), the number of complexions associated with a state in which n_1, n_2, \dots, n_c molecules occur in the c elements of volume respectively, is

$$\frac{n!}{n_1! n_2! \dots n_c!} \quad . \quad . \quad . \quad (10.1.1)$$

Hence the probability that there shall be a definite number, l , molecules in the r^{th} volume element is proportional to the sum of expressions such as (10.1.1) for all the states in which $n_r = l$, i.e., to

$$\frac{1}{l!} \sum \frac{n!}{n_1! n_2! \dots n_{r-1}! n_{r+1}! \dots n_c!} \quad (10.1.2)$$

the summation being for all positive integral values of $n_1, n_2, \dots, n_{r-1}, n_{r+1}, \dots, n_c$ consistent with

$$n_1 + n_2 + \dots n_{r-1} + n_{r+1} + \dots + n_c = n - l.$$

If $(n - l)!$ were substituted for $n!$ in the numerator, the terms in this summation would be the coefficients of the $x^\alpha y^\beta z^\gamma \dots$ products in the expansion of

$$(x + y + z + \dots \text{to } c - 1 \text{ terms})^{n-l}$$

Hence the expression (10.1.2) is equal to

$$\frac{n!}{(n-l)! l!} (c-1)^{n-l}$$

But c is a large number, and the last factor is practically c^n/c^l . Also, as we know that large deviations of l from the

average value n/c are rare, l is very much smaller than n and we can write n^l for $n(n-1)(n-2)\dots(n-l+1)$. Thus (since c^n is a constant), we find that the probability sought is proportional to

$$\frac{n^l}{c^l l!} \text{ or } \frac{a^l}{l!},$$

where a is the average value of the molecules in an element of volume. Finally, since the sum of these probabilities for all values of l is to be unity, and since the sum of the expressions $a^l/l!$ for all values of l is e^a , we see that the probability that there shall be l molecules in an element of volume, the average number being a , turns out to be

$$e^{-a} \frac{a^l}{l!} \quad . \quad . \quad . \quad . \quad . \quad (10.1.3)$$

A simple scrutiny of the result shows that $a^l/l!$ increases as l increases up to a , and thereafter decreases as l travels beyond a in value; thus there is a maximum probability for $l = a$, as there should be, of course. The average value of the deviation $l - a$ is, of course, zero, but the average value of its numerical magnitude is not. It is, as usual, estimated by means of the average value of the square of $l - a$. This will be

$$e^{-a} \sum \frac{a^l}{l!} (l - a)^2$$

$$\text{or} \quad e^{-a} \sum \left\{ \frac{l a^l}{(l-1)!} - \frac{2 a^{l+1}}{(l-1)!} + \frac{a^{l+2}}{l!} \right\}$$

By a rearrangement of terms, this can be written

$$e^{-a} \sum \left\{ \frac{(l+2) a^{l+2}}{(l+1)!} - \frac{2 a^{l+2}}{l!} + \frac{a^{l+2}}{l!} \right\}$$

$$\text{which} = e^{-a} \sum \left\{ \frac{a^{l+2}}{(l+1)!} + \frac{a^{l+2}}{l!} - \frac{2 a^{l+2}}{l!} + \frac{a^{l+2}}{l!} \right\}$$

$$= e^{-a} \sum \frac{a^{l+2}}{(l+1)!}$$

$$= a e^{-a} \sum \frac{a^{l+1}}{(l+1)!}$$

$$= a$$

Thus the mean deviation from the average value a of the number in the element is $a^{\frac{1}{2}}$. Clearly this mean deviation becomes *proportionally* less as the concentration in the element increases. For a million molecules in an element on the average, the mean deviation is a thousand either way, or one in a thousand. For a hundred million molecules in the element, the deviation is one in ten thousand. This proportional deviation measured thus, is called the "condensation," and it is clear that the average condensation in an element holding a molecules on the average is 1 in $a^{\frac{1}{2}}$ or $a^{-\frac{1}{2}}$.

Returning to (10.1.3), we see that the ratio of this expression to its maximum value is

$$\frac{a^l}{l!} \bigg/ \frac{a^a}{a!} \text{ or } \frac{a^{l-a} a!}{l!}.$$

Taking l as greater than a , this can be written

$$\frac{a. a. a. \dots a}{(a+1)(a+2)\dots l},$$

there being j factors in numerator or denominator where j is the deviation $l - a$. Hence the logarithm of this ratio is

$$-\left\{ \log\left(1 + \frac{1}{a}\right) + \log\left(1 + \frac{2}{a}\right) + \dots + \log\left(1 + \frac{j}{a}\right) \right\}$$

$$\text{which} = -\frac{1 + 2 + \dots + j}{a} + \text{negligible terms}$$

$$= -\frac{j(j+1)}{2a}$$

where, as usual, we disregard as of no importance the states where j would become more than a small fraction of a . If $l < a$ and $j = a - l$, the ratio is

$$\frac{a(a-1)\dots l}{a. a \dots a}$$

and the same result emerges for the logarithm of this ratio.

If we now wish to convert this result into a form suitable for dealing with *continuous* changes of density within a volume element rather than discrete changes in numerical

concentration, we replace $j(j+1)/2a$ by $\frac{1}{2} a \gamma^2$, where γ is the condensation in density, j/a ; for in this case unity will be negligible compared with the values of j since the average value of j is $a^{\frac{1}{2}}$ and is actually an enormous number even in a physically small element. Thus if the density ρ is given by

$$\rho = \rho_0 (1 + \gamma),$$

where ρ_0 is the average density, the probability that the density in the element lies between ρ and $\rho + \delta\rho$, *i.e.*, the condensation γ between γ and $\gamma + \delta\gamma$ is $P(\gamma) \delta\gamma$, $P(\gamma)$ being a function which satisfies

$$P(\gamma) = P_0 e^{-\frac{a\gamma^2}{2}}$$

where P_0 is the maximum value of $P(\gamma)$, occurring when $\gamma = 0$. P_0 is readily obtained from the fact that

$$\int_{-\infty}^{\infty} P(\gamma) d\gamma = 1,*$$

and by a reference to the Appendix to Chapter I., turns out to be $(a/2\pi)^{\frac{1}{2}}$. Thus the probability that the condensation is in the range γ to $\gamma + \delta\gamma$ is

$$\left(\frac{a}{2\pi}\right)^{\frac{1}{2}} e^{-\frac{a\gamma^2}{2}} \delta\gamma \quad . \quad . \quad . \quad . \quad (10.1.4)$$

a being the average number of molecules in the element. The chance of a particular condensation is smaller the greater the value of a ; this we have already deduced, but it is once more evident from (10.1.4), the decreasing exponential factor quite easily swamping the increasing factor $a^{\frac{1}{2}}$. From (10.1.4) we can once more calculate the average value of the condensation, *i.e.*, the root-mean-square condensation. It is

$$\left(\frac{a}{2\pi}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} \gamma^2 e^{-\frac{a\gamma^2}{2}} d\gamma$$

* The reader may think it absurd to integrate from negative infinity for γ , since by definition the numerically greatest value of γ , *i.e.* $(l-a)/a$, on its negative side is unity when l is zero. Fortunately we are rescued from this apparent absurdity by the fact that by the time $a\gamma^2/2$ has reached a numerical value such as 10, the outlying parts of the integral are negligible, and on account of the great value of a this is attained by quite small values of γ positive or negative.

$$\begin{aligned}\text{which} \quad &= \left(\frac{a}{2\pi}\right)^{\frac{1}{2}} \frac{1}{2} \frac{\pi^{\frac{1}{2}}}{(a/2)^{\frac{3}{2}}} \\ &= \frac{1}{a},\end{aligned}$$

so that the root-mean-square of γ is $a^{-\frac{1}{2}}$ as determined earlier. Calling the mean square value $\bar{\gamma}^2$, we can write (10.1.4) in the form

$$\frac{1}{2\pi\bar{\gamma}^2} \exp\left(-\frac{\gamma^2}{2\bar{\gamma}^2}\right) \delta\gamma.$$

10.2 Smoluchowski's Theory of the Unstable States of a Fluid.—The usual presentations of Smoluchowski's theory are so brief in the initial statements leading the fundamental equation of the theory that there is an element of obscurity and vagueness in the mind of the beginner concerning its validity. It is hoped that the following preamble will remove such doubt.

The fluctuations of density which occur throughout the body of a fluid owing to the molecular motion, imply that the volume of a given number of molecules is always varying. Instead, therefore, of considering the fluid as a molecular system, let us for the moment think of it as a continuous medium at rest in the broad sense, but pulsating throughout with compressions and rarefactions. Let us further conceive it to be divided into elements of volume, containing the same mass, which will therefore be equal if the density be truly uniform throughout. Let there be N of these elements, and for the moment let us consider that each of them is capable of having by reason of the pulsations in size any one of c discrete values of volume, v_1, v_2, \dots, v_c . (We are here, just as in Chapters I. to III., compelled to adopt in the initial stages of the reasoning the standpoint of discontinuity which will be later modified to suit the requirements of continuity.) The reader will now easily realise that a complexion of this system will be specified by saying that N_1 *particular* elements have a volume v_1 , N_2 *particular* elements a volume v_2 , etc. The number of complexions is as usual $N!/N_1! N_2! \dots N_c!$ for the statistical state

N_1, N_2, \dots, N_c . As usual, this will be assumed to be proportional to the probability of the occurrence of the state.

To find the most probable state, we proceed as before, taking account of the energy condition. This condition is obtained in the following manner. If v_o is the volume of any element at uniform density throughout, and p_o the uniform pressure then existing, the potential energy in an element of the fluid at volume v , over and above the energy at volume v_o is

$$\int_{v_o}^{v_r} (p_o - p) dv \quad . \quad . \quad . \quad . \quad (10.2.1)$$

p being the pressure at volume v . To justify this, remember that if v is smaller than v_o , p is greater than p_o , and so work would have to be done *on* the element to force it into a smaller volume than that consistent with a pressure p_o from its environment. (The case is analogous to that of a body suspended at the end of a spring. If the tension T at a length l is greater than the weight w , then work has to be done in forcing the body down to this length of the spring.) This work is the product of $p - p_o$, and the *decrease* in volume, *i.e.*, the product of $p_o - p$ and δv . If, on the other hand, v is larger than v_o and p less than p_o , work still has to be done on the element to force it out into a larger volume than that consistent with the pressure p_o . (Again, there is the analogy of the body being higher than its mean position, there being a reduced energy of extension of the spring, but a more than compensating gain in the gravitational energy of the body.) The work done is the product of $p_o - p$, and the *increase* in volume, *i.e.*, $(p_o - p) \delta v$. As in the case of a body oscillating up and down there is increase of potential energy whether the body is above or below its mean position, so in the pulsating element of volume there is increased potential energy whether the size of the element is greater or less than v_o . The reader will naturally think of the accompanying changes of kinetic energy which would accompany such oscillations and pulsations in *isolated* systems; but he is asked to bear in mind that we are counting complexions consistent *with constant temperature throughout, i.e.*,

changes in kinetic energy are ruled out by that proviso, and the energy condition to be satisfied is that gains in the potential energy of certain elements are to be compensated by losses in the others, or, in short, if we represent (10.2.1) by ϵ_r ,

$$N_1 \epsilon_1 + N_2 \epsilon_2 + \dots + N_c \epsilon_c = \text{constant}.$$

Combined with the condition of a constant sum for the N_r , we have the same solution as before. In the most probable state of the pulsating medium the number of elements whose volume will be v_r at any instant is proportional to $\exp(-\eta \epsilon_r)$, where η is a constant to be determined from the condition of constant number and potential energy.

The equation of state of the fluid enables us to express (10.2.1) as a function of v_r . (It may be as well to point out at this juncture, in view of the warning issued some pages back, that in (10.2.1) p is the external pressure; the calculation of work done on and by the element in its changes ensures that.) If a, b, c , etc., stand for the partial differential coefficients $\partial p / \partial v$, $\partial^2 p / \partial v^2$, $\partial^3 p / \partial v^3$, etc., all estimated at the value v_0 for v , and, of course, at constant temperature, then we know by Taylor's theorem that

$$p = p_0 + \frac{a}{1!} (v - v_0) + \frac{b}{2!} (v - v_0)^2 + \frac{c}{3!} (v - v_0)^3 + \dots$$

and thus by (10.2.1)

$$\epsilon_r = - \left\{ \frac{a}{2!} (v_r - v_0)^2 + \frac{b}{3!} (v_r - v_0)^3 + \frac{c}{4!} (v_r - v_0)^4 + \dots \right\}$$

We can now adapt the preceding considerations to the idea that the volume of an element changes continuously, and not by discrete amounts. The number of elements which in the most probable state have a volume between v and $v + \delta v$ is given by

$$D \exp \{ \eta \psi(v) \} \delta v,$$

where

$$\psi(v) = \frac{a}{2!} (v - v_0)^2 + \frac{b}{3!} (v - v_0)^3 + \frac{c}{4!} (v - v_0)^4 + \dots$$

and D and η are constants to be determined from

$$D \int_0^\infty e^{\eta \psi} dv = N$$

$$D \int_0^\infty \psi e^{\eta \psi} dv = \text{constant}.$$

Instead of the variable v , we can introduce the condensation, γ , defined as $(v_0 - v)/v_0$. The number of elements which in the most probable state have a value of condensation between γ and $\gamma + \delta\gamma$ is proportional to

$$\exp\{\eta \phi(\gamma)\} \delta\gamma,$$

where

$$\phi(\gamma) = A\gamma^2 + B\gamma^3 + C\gamma^4 + \dots \quad (10.2.2)$$

A, B, C, \dots being coefficients given by

$$A = \frac{1}{2!} v_0^2 \left(\frac{\partial^2 p}{\partial v^2} \right)_0$$

$$B = \frac{1}{3!} v_0^3 \left(\frac{\partial^3 p}{\partial v^3} \right)_0 \quad . \quad . \quad . \quad (10.2.3)$$

$$C = \frac{1}{4!} v_0^4 \left(\frac{\partial^4 p}{\partial v^4} \right)_0$$

$$\begin{matrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{matrix}$$

If now we suppose that our attention is concentrated on one element of the fluid, we can assume the probability that at a given moment the condensation in this element has a value between γ' and γ'' to be proportional to the number of elements which at any time have in the most probable state condensations within these limits. This probability is therefore proportional to

$$\int_{\gamma'}^{\gamma''} \exp\{\eta \phi(\gamma)\} d\gamma.$$

We can find the value of η directly by a reference to the result (10.1.4) in the previous section. In the case of gases in a rare state for which one would anticipate that the analysis of that section holds, the molecules exerting no action on one another on the average, it appears that $\eta \phi(\gamma)$

should be equal to $-a\gamma^2/2$, where a is the average number of molecules in the element of volume. Also as only relatively small values of γ are effective in actual fact, we can ignore γ^3 and higher powers of γ in the series for $\phi(\gamma)$ in the case contemplated. Hence

$$\begin{aligned} \eta A \gamma^2 &= -a \gamma^2/2 \\ \text{or} \quad \eta &= -\frac{a}{2} \left/ \left\{ \frac{v_o^2}{2!} \left(\frac{\partial p}{\partial v} \right) \right\} \right. \\ &= -\frac{a}{v_o^2} \left/ \left(-\frac{a k \theta}{v_o^2} \right) \right. \quad \text{since } p = \frac{a k \theta}{v} \\ &= \frac{1}{k \theta} \\ &= \mu. \end{aligned}$$

Once more the distribution constant emerges and Smoluchowski's result is written

$$\int_{-\infty}^{\infty} \exp\{\mu \phi(\gamma)\} d\gamma \quad . \quad . \quad . \quad (10.2.4)$$

The author trusts that the rather lengthy exposition is justified. Most accounts start baldly with the assumption that the probability in question is given by an expression involving

$$e^{-\frac{E}{k\theta}} dv,$$

where $E = \int_{v_o}^v (p - p_o) dv$, with no very clear reason given for this value.*

In order to apply the result to other states of the fluid than that of rare gas, we first of all note that if $(\partial p / \partial v)_o$ is negative, the index in the exponential factor of the probability is essentially negative for any value of γ positive or negative, giving decreasing probability for increasing fluctuations, obviously a necessity of any stable state. If,

* It will be perhaps wise to warn the reader that E is more usually written

$$m a \int_{v_o}^v (p - p_o) dv,$$

but that is because v is then the *specific* volume of the fluid, and so the factor, ma , the mass of the fluid in an element of volume is required. In the text v is the volume of the element.

however, $(\partial p/\partial v)_0$ is positive in the state of uniform distribution—and we have seen the theoretical possibility of this—the exponent is positive for any value of γ , giving increasing probability for increasing condensation or rarefaction; in short, the state is highly unstable, and so the general inference drawn before is amply confirmed by this closer analysis. It will be remembered that on a Van der Waal's isotherm there may be two points where $\partial p/\partial v$ is zero. If the average density of a fluid should correspond to either of these points, the series for $\phi(\gamma)$ would start with γ^3 , and ignoring the remaining terms of the series, the probability would involve

$$\exp(\mu B \gamma^3)$$

Thus, according to the sign of $\partial^2 p/\partial v^2$, we would have increasing probability for fluctuations involving expansion, and decreasing probability for fluctuations involving contraction or *vice versa*. This one-sided stability would be useless for maintaining a physically homogeneous state. Indeed, there are parts of the isothermals where $\partial p/\partial v$ is negative, but which are so near to the points just mentioned that they can hardly be said to correspond to stability in a real physical sense, since they are associated with super-saturated vapour or superheated liquid. Smoluchowski's result is quite consistent with this; for a negative but *small* value of A in $e^{\mu A \gamma^3}$ means that γ must increase numerically more than usual before one goes beyond ordinary probabilities, and by that time the fluid in an element may, if the fluctuation has been in the suitable sense, have attained the highly unstable condition.

But perhaps the most interesting application of Smoluchowski's theory concerns the critical state at which $\partial p/\partial v$ and $\partial^2 p/\partial v^2$ are both zero. In that case both A and B are zero, and the series for $\phi(\gamma)$ begins with $C\gamma^4$. To determine the stability of this state we must determine a value for C . This can at all events be obtained approximately from Van der Waal's equation, which we write

$$p = \frac{ak\theta}{v - \beta} - \frac{a}{v^2}.$$

(We are using a for the cohesion constant, since a is being used as the average number of molecules in an element of volume, and β for the minimum volume.)

Thus

$$\frac{\partial^3 p}{\partial v^3} = -\frac{6ak\theta}{(v-\beta)^4} + \frac{24a}{v^5},$$

and by (10.2.3)

$$C = \frac{a}{v} - \frac{ak\theta v^4}{4(v-\beta)^4}$$

At the critical point it is known (since $\partial p/\partial v$ and $\partial^2 p/\partial v^2$ are zero there) that $v = 3\beta$, $p = a/27\beta^2$ and $ak\theta = 8a/27\beta$. Thus at that point

$$\begin{aligned} C &= \frac{a}{3\beta} - \frac{81ak\theta}{64} \\ &= \frac{9ak\theta}{8} - \frac{81ak\theta}{64} \end{aligned}$$

or
$$\mu C = -\frac{9a}{64}$$

The series for $\phi(\gamma)$ now starts with γ^4 , and neglecting higher powers, the probability now involves the exponential factor

$$\exp\left(-\frac{9a}{64}\gamma^4\right).$$

As this decreases with any variation of γ from zero, the critical state is stable; but closer investigation shows that the condensation fluctuates between wider values than in other conditions. This is proved by working out an average value for γ . Thus the average value of the positive condensations is (writing c for $9a/64$)

$$\frac{\int_0^\infty e^{-c\gamma^4} \gamma d\gamma}{\int_0^\infty e^{-c\gamma^4} d\gamma},$$

which, by writing x for $c^{\frac{1}{4}}\gamma$, becomes

$$\frac{c^{-\frac{1}{4}} \int_0^\infty e^{-x^4} x dx}{c^{-\frac{1}{4}} \int_0^\infty e^{-x^4} dx}$$

The integral in the numerator is $\frac{1}{2} \int_0^\infty e^{-y^2} dy$, which is, as we know, $\pi^{1/4}/2$; the integral in the denominator can be calculated by quadrature to be $0.666 \dots$, and so we obtain finally for the average value of the positive condensation

$$\frac{1.13}{a^{\frac{1}{4}}}$$

It is the appearance of the fourth root of a , and not the square root, as in the case of gases in a more usual condition, which is the interesting feature. Thus, in an element of volume containing 10^8 molecules, which for a substance in the critical state would have linear dimensions of the order of magnitude of the wavelengths of light, the value of this expression would be about $\cdot 01$, and so fluctuations in size of the order of 1 per cent. in density would be the average sort of occurrence. It is this result which is held to account for the well-known opalescence which appears in a substance in the critical condition; the real lack of homogeneity in the medium is sufficiently marked to scatter the light of a beam which is passed through it. When the illumination is strong, a scattering of bluish light can be observed in a direction at right angles to the beam. Keesom has, in fact, linked up Smoluchowski's theory with physical optics, and deduced the well-known formula of Rayleigh for the intensity of the blue light of the sky, thus connecting this phenomenon with fluctuation theory.

CHAPTER XI

THE SECOND LAW OF THERMODYNAMICS. II

11.1 The Thermodynamical Equilibrium of a Condensed System.—In Chapter VI. we deduced the second law of thermodynamics for a gaseous phase in statistical equilibrium. It is necessary to make sure that the deduction is still valid for systems in which we cannot ignore intermolecular action.

As we have seen in Chapter IX., the normal state of a system, for which the energy is given by a general function $f(n_1, n_2, \dots, n_c, a_1, a_2, \dots, a_c)$ of the numbers in the phase-cells and the parameters, is obtained from the equations

$$f(n_1, n_2, \dots, n_c, a_1, a_2, \dots, a_c) = E$$

$$n_1 + n_2 + \dots + n_c = n \quad . \quad . \quad (11.1.1)$$

and the c equations, $\log n_r = \lambda - \mu \frac{\partial f(n, a)}{\partial n_r}$.

These may be regarded as $c + 2$ equations to determine λ , E and each of the n_r as functions of μ and the c parameters a_1, a_2, \dots, a_c . We shall denote the functions so determined by $\lambda(\mu, a)$, $H(\mu, a)$, $v_1(\mu, a)$, $\dots, v_c(\mu, a)$. $H(\mu, a)$ is, of course, obtained from $f(n, a)$ by inserting the c functions $v_r(\mu, a)$ in place of the variables, n_r ; i.e.,

$$H(\mu, a) = f(v_1, v_2, \dots, v_c, a_1, a_2, \dots, a_c) \quad . \quad (11.1.2)$$

Let us also denote by $\chi_r(\mu, a)$ the function obtained when the functions $v_1(\mu, a)$, $v_2(\mu, a)$, etc., are substituted for n_1, n_2 , etc., in $\partial f(n, a)/\partial n_r$, and by $\zeta_s(\mu, a)$, the function obtained when the same substitution is made in $\partial f(n, a)/\partial a_s$.

It follows that

$$\frac{\partial H(\mu, a)}{\partial \mu} = \sum_{r=1}^c \chi_r \frac{\partial v_r}{\partial \mu} \quad . \quad . \quad (11.1.3)$$

and
$$\frac{\partial H(\mu, a)}{\partial a_s} = \sum_{r=1}^c \chi_r \frac{\partial v_r}{\partial a_s} + \zeta_s(\mu, a) \quad . \quad . \quad (11.1.4)$$

Recalling the general line of argument in Chapter VI., we consider a change from a normal state with values μ, a for the S.M. variables to a normal state with values $\mu + \delta\mu, a + \delta a$. The change of energy δE which is given by

$$\delta E = \frac{\partial H(\mu, a)}{\partial \mu} \delta\mu + \sum_{s=1}^c \frac{\partial H(\mu, a)}{\partial a_s} \delta a_s \quad . \quad (11.1.5)$$

is, as before, separated into two parts, one of which, δE_1 , is the change accompanying a variation in the parameters, *but with the distribution in the phase-cells still left at the original normal distribution*. The remainder is δE_2 . It should be noted that δE_1 , the analogue of the mechanical work alone done on the system, is not given by the second term on the right-hand side of (11.1.5), as a glance at (11.1.4) will show. Actually

$$\begin{aligned} \delta E_1 &= \sum_{s=1}^c \zeta_s(\mu, a) \delta a_s \\ &= \sum_{s=1}^c \frac{\partial H(\mu, a)}{\partial a_s} \delta a_s - \sum_{r=1}^c \sum_{s=1}^c \chi_r \frac{\partial v_r}{\partial a_s} \delta a_s \quad . \quad (11.1.6) \end{aligned}$$

To proceed successfully from this point, our aim, as in Chapter VI., must be to discover a function $\Psi(\mu, a)$, such that

$$\delta E_1 = \sum_{s=1}^c \frac{\partial \Psi(\mu, a)}{\partial a_s} \delta a_s \quad . \quad . \quad (11.1.7)$$

and with that end in view, we write (11.1.6) as

$$\delta E_1 = \sum_{s=1}^c \frac{\partial}{\partial a_s} \left\{ H(\mu, a) - \sum_{r=1}^c \chi_r v_r \right\} \delta a_s + \sum_{r=1}^c \sum_{s=1}^c v_r \frac{\partial \chi_r}{\partial a_s} \delta a_s \quad (11.1.8)$$

and endeavour to adapt the last term in this to the necessary form. Guided by the procedure in Chapter VI., we obtain from (11.1.1) the following equations, which are identically true for any values of the a_s

$$\log v_r(\mu, a) = \lambda(\mu, a) - \mu \chi_r(\mu, a) \quad . \quad (11.1.9)$$

Differentiating this with respect to any of the a_s yields an identity

$$\frac{\partial v_r}{\partial a_s} = v_r \frac{\partial \lambda}{\partial a_s} - \mu v_r \frac{\partial \chi_r}{\partial a_s}$$

and an addition of these gives

$$\mu \sum_{r=1}^c v_r \frac{\partial \chi_r}{\partial a_s} = n \frac{\partial \lambda}{\partial a_s} \quad \text{since} \quad \frac{\partial n}{\partial a_s} = 0.$$

On substituting in (11.1.8), we find that (11.1.7) is valid if we define $\Psi(\mu, a)$ thus

$$\Psi(\mu, a) = H(\mu, a) - \sum_{r=1}^c \chi_r(\mu, a) v_r(\mu, a) + n \frac{\lambda(\mu, a)}{\mu} \quad (11.1.10)$$

This is obviously a generalisation of the definition in Chapter VI.; for if $f(n, a)$ is linear in the n_r , $f(n, a) = \sum n_r \partial f / \partial n_r$, and thus $H(\mu, a) = \sum \chi_r v_r$; so that in such case Ψ reduces to $n \lambda / \mu$.

However, we have not carried the attempt to a successful conclusion yet. We must also see if the mathematical relation (6.2.7) in Chapter VI. is still valid. Naturally we follow the same procedure as we did there and differentiate the identities (11.1.9) with respect to μ , thus obtaining

$$\frac{\partial v_r}{\partial \mu} = v_r \frac{\partial \lambda}{\partial \mu} - v_r \chi_r - \mu v_r \frac{\partial \chi_r}{\partial \mu}.$$

Addition of these c relations yields

$$n \frac{\partial \lambda}{\partial \mu} = \sum_{r=1}^c v_r \chi_r + \mu \sum_{r=1}^c v_r \frac{\partial \chi_r}{\partial \mu} \quad . \quad . \quad (11.1.11)$$

From (11.1.10) we obtain

$$\frac{\partial \Psi(\mu, a)}{\partial \mu} = \frac{\partial H(\mu, a)}{\partial \mu} - \sum_{r=1}^c v_r \frac{\partial \chi_r}{\partial \mu} - \sum_{r=1}^c \chi_r \frac{\partial v_r}{\partial \mu} + \frac{n}{\mu} \frac{\partial \lambda}{\partial \mu} - n \frac{\lambda}{\mu^2}.$$

which by (11.1.3) and (11.1.11)

$$= \frac{1}{\mu} \sum_{r=1}^c v_r \chi_r - n \frac{\lambda}{\mu^2},$$

and by (11.1.10)

$$= \frac{H(\mu, a) - \Psi(\mu, a)}{\mu} \quad . \quad . \quad (11.1.12)$$

Thus, as before,

$$\begin{aligned}
 \delta E_2 &= \delta E - \delta E_1 \\
 &= \delta H(\mu, a) - \sum_{s=1}^c \frac{\partial \Psi(\mu, a)}{\partial a_s} \delta a_s \\
 &= \delta H(\mu, a) - \left\{ \delta \Psi(\mu, a) - \frac{\partial \Psi(\mu, a)}{\partial \mu} \delta \mu \right\} \\
 &= \delta \left\{ H(\mu, a) - \Psi(\mu, a) \right\} + \frac{H(\mu, a) - \Psi(\mu, a)}{\mu} \delta \mu
 \end{aligned}$$

and

$$\mu \delta E_2 = \delta \left[\mu \{ H(\mu, a) - \Psi(\mu, a) \} \right].$$

The general line of argument proceeds as before to a deduction of the second law with the entropy defined by

$$\Phi(\mu, a) = k \mu \{ H(\mu, a) - \Psi(\mu, a) \},$$

for the relations (11.1.9) give us

$$\begin{aligned}
 \log W_m &= n \log n - \sum_{r=1}^c \nu_r \log \nu_r \\
 &= n \log n - n \lambda + \mu \sum_{r=1}^c \nu_r \chi_r,
 \end{aligned}$$

so that

$$\begin{aligned}
 k (\log W_m - n \log n) &= k \mu \{ H(\mu, a) - \Psi(\mu, a) \} \\
 &= \Phi(\mu, a),
 \end{aligned}$$

and the connection between increasing entropy and increasing probability is once more established.

CHAPTER XII

THE STATISTICAL-MECHANICAL THEORY OF A LIQUID AND A VAPOUR PHASE IN CONTACT

12.1 Deduction of Clapeyron's Equation.—An enclosure of given volume is supposed to have a portion of its volume V_1 occupied by a saturated vapour and the remainder V_2 occupied by the liquid; the number of molecules in the vapour is n_1 and n_2 in the liquid, so that the concentrations are given by $\nu_1 = n_1/V_1$ and $\nu_2 = n_2/V_2$. In Chapter IX. it was demonstrated that under these circumstances

$$\begin{aligned}\nu_1 &= D \left(\frac{\mu}{2\pi m} \right)^{\frac{3}{2}} e^{-\mu\phi(\nu_1)} \quad . \quad . \quad . \quad (12.1.1) \\ \nu_2 &= D \left(\frac{\mu}{2\pi m} \right)^{\frac{3}{2}} e^{-\mu\phi(\nu_2)}\end{aligned}$$

where $\phi(\nu)$ is the potential energy of one molecule due to intermolecular force in a place where the concentration is ν . This result is not dependent on any particular functional form for ϕ ; but it will be found as we proceed that we must have a modicum of information about it in order to come to a definite conclusion in the problem on which we are engaged. First of all we know that $\phi(\nu)$ approaches a maximum value as ν decreases, and beyond a certain concentration it is practically constant; so that in the gaseous phase we shall assume that $\phi'(\nu)$ is zero, where $\phi'(\nu)$ is written for $d\phi(\nu)/d\nu$. As ν increases and the molecules approach one another on the average, the potential diminishes so long as the forces are attractive. But when the liquid state is reached, the average separation is such that there is a compensation between attractions and repulsions on the average, and further compression would involve an increase of the potential energy due to preponderance of repulsive force. So that the concentrations in the liquid state would be such

that for any value of ν in the narrow range involved, $\phi(\nu)$ would practically be a minimum, so that $\phi'(\nu)$ would be practically zero in this case also. Thus in order to give the necessary definiteness to our problem, we shall assume that the function ϕ satisfies for the two phases in question

$$\phi'(\nu_1) = 0 \quad \phi'(\nu_2) = 0 \quad . \quad . \quad . \quad (12.1.2)$$

By reason of (12.1.1.)

$$\nu_1 e^{\mu\phi(\nu_1)} = \nu_2 e^{\mu\phi(\nu_2)}$$

or

$$\log n_1 + \mu\phi(\nu_1) - \log V_1 = \log n_2 + \mu\phi(\nu_2) - \log V_2.$$

Now consider the system with a slightly altered distribution constant, *i.e.*, temperature; this will involve an alteration in the numbers and concentrations as well as in the volumes V_1 and V_2 . Differentiating with respect to the temperature θ , and remembering that $d\mu/d\theta = -1/k\theta^2$, we obtain

$$\begin{aligned} \frac{1}{n_1} \frac{dn_1}{d\theta} - \frac{1}{V_1} \frac{dV_1}{d\theta} + \mu\phi'(\nu_1) \frac{d\nu_1}{d\theta} - \frac{\phi(\nu_1)}{k\theta^2} \\ = \frac{1}{n_2} \frac{dn_2}{d\theta} - \frac{1}{V_2} \frac{dV_2}{d\theta} + \mu\phi'(\nu_2) \frac{d\nu_2}{d\theta} - \frac{\phi(\nu_2)}{k\theta^2} \end{aligned}$$

so that, on account of the hypothesis we make as regards an ideal liquid and vapour state in (12.1.2),

$$\frac{1}{n_1} \frac{dn_1}{d\theta} - \frac{1}{n_2} \frac{dn_2}{d\theta} - \frac{1}{V_1} \frac{dV_1}{d\theta} + \frac{1}{V_2} \frac{dV_2}{d\theta} = \frac{1}{k\theta^2} \{ \phi(\nu_1) - \phi(\nu_2) \} \quad (12.1.3)$$

We can simplify this result very markedly by assuming that the two phases occupy equal parts of the enclosure at the temperature θ . Since the enclosure has a *fixed* volume $dV_1/d\theta = -dV_2/d\theta$, and if we now also assume that V_1 is equal to V_2 , the two terms involving these quantities disappear. Further under such circumstances

$$\frac{n_1}{n_2} = \frac{v_2}{v_1}$$

where v_1 and v_2 are the *specific volumes* of the two phases, since $n_1 v_1 m$ and $n_2 v_2 m$ are equal respectively to V_1 and V_2 .

Lastly, since the total number of molecules is constant, $dn_1/d\theta = -dn_2/d\theta$, and so the left-hand side of (12.1.3) becomes

$$\left(\frac{1}{n_1} - \frac{1}{n_2}\right) \frac{dn_1}{d\theta},$$

which

$$\begin{aligned} &= \left(1 - \frac{v_2}{v_1}\right) \frac{1}{n_1} \frac{dn_1}{d\theta} \\ &= \left(1 - \frac{v_2}{v_1}\right) \frac{1}{v_1} \frac{dv_1}{d\theta} \\ &= \left(1 - \frac{v_2}{v_1}\right) \frac{d \log v_1}{d\theta}. \end{aligned}$$

On the right-hand side of (12.1.3), $\phi(v_1) - \phi(v_2)$ is the energy required to remove one molecule from the liquid phase to the vapour, and since the volume of the enclosure is fixed, and therefore no external work performed, this is the *internal* heat of vaporisation per molecule. Denoting it by w , we have, as the final result

$$\left(1 - \frac{v_2}{v_1}\right) \frac{d \log v_1}{d\theta} = \frac{w}{k\theta^2} \quad . \quad . \quad . \quad (12.1.4)$$

and this leads directly to Clapeyron's equation, for if p is the vapour pressure,

$$\begin{aligned} p &= v_1 k\theta \\ \text{and} \quad \frac{d \log p}{d\theta} &= \frac{d \log v_1}{d\theta} + \frac{1}{\theta} \\ &= \frac{v_1}{v_1 - v_2} \frac{w}{k\theta^2} + \frac{1}{\theta} \\ &= \frac{v_1}{v_1 - v_2} \left\{ \frac{L_i}{R\theta^2} + \frac{v_1 - v_2}{v_1} \frac{R\theta}{R\theta^2} \right\} \end{aligned}$$

where L_i is the internal latent heat of n molecules and $R = nk$. Since the first phase is considered to be an ideal gas, $R\theta = pv_1$, and so

$$\begin{aligned} \frac{d \log p}{d\theta} &= \frac{v_1}{v_1 - v_2} \frac{L_i + p(v_1 - v_2)}{R\theta^2} \\ &= \frac{v_1}{v_1 - v_2} \frac{L}{R\theta^2}, \end{aligned}$$

where L is the ordinary latent heat. As v_2 is small compared to v_1 , we have approximately

$$\frac{d \log p}{d\theta} = \frac{L}{R\theta^2},$$

but keeping the exact equation, and once more writing pv_1 for $R\theta$, we obtain

$$\frac{d \log p}{d\theta} = \frac{L}{p\theta(v_1 - v_2)}$$

or
$$\frac{dp}{d\theta} = \frac{L}{\theta(v_1 - v_2)} \quad . \quad . \quad . \quad (12.1.5)$$

which is the proper result, and as a matter of fact, is the *exact* equation deducible by strictly thermodynamical reasoning for real liquids and vapours.

12.2 The Relation between the Latent Heat and the Specific Heats.—The second thermodynamic equation for a liquid-vapour system can now be easily obtained. Let s_1 and s_2 be the specific heats of the vapour and the liquid, it being understood that these are the thermal capacities of unit mass of the vapour or liquid as heated in the fixed enclosure (not subjected to a constant pressure nor on the other hand with each portion maintained at constant volume, the usual conditions). The proviso is well known to those acquainted with the thermodynamical treatment of this matter. The vapour, for instance, is maintained in a saturated condition during the heating, involving a diminution of volume, and on that account it may happen that if the external work thus performed on the vapour is too great, heat would have to be removed from the vapour, and s_1 would be negative. This is in fact the case with water. In the case of the liquid, s_2 differs but little from the usual specific heat under constant external pressure.

If now unit mass of the liquid is heated through $\delta\theta$, the heat supplied is $s_2\delta\theta$, and external work $p\delta v_2$ is performed. Thus the internal energy of the unit mass of liquid is greater by $s_2\delta\theta - p\delta v_2$. If unit mass of the vapour is similarly heated, its energy increases by $s_1\delta\theta - p\delta v_1$. (As just mentioned, δv_1 is in general a negative quantity if $\delta\theta$ is

positive.) Hence the energy difference between the liquid and vapour phase increases during the change of temperature by

$$s_1\delta\theta - p\delta v_1 - s_2\delta\theta + p\delta v_2.$$

But this energy difference is L_i at first, and after the temperature rise $L_i + \delta L_i$, so

$$\frac{dL_i}{d\theta} = s_1 - s_2 - p \frac{d(v_1 - v_2)}{d\theta}.$$

Hence

$$\frac{d\{L_i + p(v_1 - v_2)\}}{d\theta} = s_1 - s_2 + (v_1 - v_2) \frac{dp}{d\theta}$$

and thus, by Clapeyron's equation

$$\frac{dL}{d\theta} - \frac{L}{\theta} = s_1 - s_2 \quad . \quad . \quad . \quad (12.2.1)$$

To be sure by our hypothesis (12.1.2)

$$\begin{aligned} \frac{dw}{d\theta} &= \phi'(v_1) \frac{dv_1}{d\theta} - \phi'(v_2) \frac{dv_2}{d\theta} \\ &= 0, \end{aligned}$$

and L_i will not change with temperature at all for our ideal liquid, which is a rather restrictive hypothesis.

CHAPTER XIII

THE SOLID STATE CONSIDERED AS A SIMPLE LATTICE OF MASSIVE PARTICLES

13.1 The Specific Heat of a Monatomic Solid.—We now come to the treatment on classical lines of the last topic to be dealt with before an endeavour is made to introduce the reader to the modifications of statistical-mechanical theory occasioned by the quantum hypothesis. On classical lines it lends itself to very simple treatment indeed.

The rigidity of a solid, which is its characteristic feature, we shall idealise by conceiving it as constituted of a group of n particles, each of mass m , situated at the points of a simple space-lattice, so that choosing three axes of reference in a suitable manner, the co-ordinates of any particle are given by ja, kb, lc , where a, b, c are three elementary lengths and j, k, l are integers—at least, that is assumed to be the state of affairs at absolute zero of temperature with no thermal motion going on, each particle being held firmly to its equilibrium position by the forces arising from its neighbours. The particles are regarded as without structure; so the model is “monatomic.” If energy is given to the system, each particle will vibrate about its mean position, the displacements at any moment parallel to the axes being represented by ξ, η, ζ , and the velocity-components by $\dot{\xi}, \dot{\eta}, \dot{\zeta}$. If we make the well-known simple assumption that the elastic forces on a particle set up by the displacements are towards the equilibrium position and proportional to the displacement, the motion of each particle is simple harmonic. The energy is a quadratic function of the $3n$ co-ordinates (ξ_r, η_r, ζ_r), and the $3n$ momenta ($m \dot{\xi}_r, m \dot{\eta}_r, m \dot{\zeta}_r$), involving squares alone. The application of the statistical method follows the usual course, with a phase-diagram, in which are represented these $3n$ co-ordinates and $3n$ momenta, par-

tioned into phase-cells. Counting of complexions, determination of the most probable state, etc., lead to the usual type of solution as to the number of representative points in a phase-cell, this number depending as ever on $e^{-\mu\epsilon}$ where ϵ is the energy corresponding to the centre of the phase-cell, and is, of course, the sum of kinetic and potential parts. The distribution constant μ , is still connected with the temperature by the relation $k\theta = \mu^{-1}$. To see this we can consider the solid immersed in a simple gas; in the normal state they will have the same distribution-constant for the simple reason pointed out earlier in the treatment of mixtures of gases and of internal degrees of freedom in gas molecules. As energy is freely interchangeable between all molecules, gaseous or solid, there is only one variational equation for the energy, and thus only one multiplier, μ , is involved for this equation in the solution by the method of indeterminate multipliers. By means of the pressure equation, we, as usual, identify the temperature of the gas as $(k\mu)^{-1}$, and, of course, in equilibrium, the solid has the same temperature.

A conclusion of great importance follows, as in Chapter V., viz., the equipartition on the average of the energy between the various components of displacement and of momenta, $\frac{1}{2} k\theta$ for each component, this being due to the absence of all but squared terms in the expression for the total energy. Thus it follows directly that the total energy is $6n$ times this elementary amount, or $3nk\theta$. Hence the thermal capacity of the solid should be $3nk$. For a gram-molecule, this is $3R$ where R is the gram-molecular gas-constant. This works out about 5.95 calories per degree. This well-known law, first pointed out by Dulong and Petit, is actually a good approximation to the truth for many monatomic solids, provided the temperature is sufficiently high, but the inference that the specific heat is independent of the temperature, is violently at variance with the facts. Just as in the case of diatomic gases there arises a serious discrepancy which classical statistical-mechanical theory has never been able to remove. The reader may think that our simple hypotheses are too restrictive; but although with wider

conceptions as to the dependence of potential energy on displacement, we would obtain a different partition of the energy, the constancy of the specific heat as regards change of temperature would still emerge from the treatment, and this is an untenable conclusion, an asymptotic fall of thermal capacity to zero as the temperature approaches absolute zero being one of most striking experimental facts discovered within the last twenty years.

The removal of this discrepancy and the discovery of a satisfactory formula for the specific heat of a monatomic solid has, as stated, been effected by means of the quantum hypothesis. It is time to turn our attention to this way of escape from the various difficulties which have met us at several points on our way hither.

CHAPTER XIV

THE QUANTUM HYPOTHESIS

14.1 The Three Stages in the History of the Quantum Theory.—The first suggestion of the momentous change which has taken place in Theoretical Physics during the present century, was made in 1900, when Planck, in order to clear away a discrepancy between the experimental facts of black body radiation and the conclusions deduced from the current dynamical and electrodynamical theory, introduced the idea that the mechanism within an atom responsible for the emission and absorption of radiant energy, did not carry out this process in the continuous manner consistent with the laws of dynamics and of Maxwell's electromagnetic theory, but in a discontinuous and "catastrophic" manner. It must be admitted that the reception of this notion was rather chilly; in the mental atmosphere of that time anything which savoured of the "revolutionary" was frowned on; Einstein had not as yet arrived. But he soon did; in 1905, the very year which saw his first paper on the Relativity theory, he gave decided evidence of the fact that he always has been interested in other things in Physics besides the theory of space and time—a fact not too widely known to the "popular" scientific public. He carried Planck's suggestion a step further and a very "shocking" step it was, even to those who were by that time prepared to listen to Planck. It introduced the idea of "atomicity" into radiation not merely in its moments of absorption and emission by matter, but also in its propagation through space. Despite the fact that it led to an immediate advance in the study of phenomena, such as fluorescence and the photoelectric effect, it was too much for the general scientific world, and it is only now just as the foundations of a real consistent Quantum theory have been laid down, that we

can appreciate that Einstein's "light-quantum" idea was one of those flashes of insight vouchsafed now and then to the man of genius. Even so, Einstein did show two years later that Planck's suggestion in its original and less upsetting form could be applied to the elucidation of the theoretical difficulties which statistical mechanics encounters in dealing with specific heats. Planck, in addition, demonstrated a rather unexpected link between his hypothesis and the heat theorem of Nernst (the so-called third law of Thermodynamics), which was playing a great part in Physical Chemistry at this period. Planck, however, was no "revolutionary," and was also busy in recasting his original presentation of the quantum idea, so as to soften as far as possible the break with traditional conceptions. In 1912 Debye and Born had subjected the whole problem of the specific heats of monatomic solids to a most searching mathematical analysis in the manner suggested by Einstein in 1907, and the result was a triumphant vindication of the power of this new weapon. The trouble concerning the specific heats of diatomic gases was also showing clear signs of yielding to the "new treatment." The leading physicists of the world were at last in their congresses and contributions to journals displaying the keenest interest in the "mystery of quantum."

The second period in this eventful history was ushered in by three papers contributed by Bohr to the *Philosophical Magazine* in 1913. In them was first propounded the theory of the "Stationary States of an Atom," a theory which was the clear descendant of Planck's first form of the Quantum hypothesis and not the second. This period has been marked by the development of an uneasy partnership between the classical laws of dynamics and electrodynamics and two postulates of Bohr's, one a flat denial of a particular result in classical electron theory, the other, an ingenious modification of Planck's law of emission for his "oscillator." The hostile partners have been driven in harness together, and "made to behave" by means of another ingenious notion of Bohr's, the "Principle of Correspondence." This patchwork affair has, despite the incongruity of the situation,

been at once incentive and guide during a dozen years amazingly fertile in theoretical investigation and experimental research. The debt which experimental physics owes to this "Classical-Quantum theory" is large beyond question; yet equally certain is it that this was not a "theory" in the accepted sense of a perfectly consistent body of principles from which all the essential experimental facts could be deduced. This period closed in the autumn of 1925, when Heisenberg, in a paper which will probably rank with Einstein's first relativity paper of 1905, as an epoch-making communication, pointed clearly the direction in which we had to go for a genuine escape from all our theoretical doubts and misgivings. Then began the third period, a period of the construction of a genuine Quantum theory of atomic phenomena. Already in four years physicists can feel that their science is based once more on a foundation which, although not as yet complete, is as far as it goes firm and self-consistent. To the philosophical mind it is of interest to observe one common feature of Heisenberg's contribution to the theory of the microcosm which we call the atom and Einstein's contribution to the theory of the large-scale phenomena of the "world." Einstein pointed out that we were unduly hampering our ideas by trying to reconcile the independence of the velocity of light with respect to the frame of observation and the assumption of an absolute space; as the former is a physical fact, he suggested that the latter should be abandoned and the mathematical treatment suitably modified, and proceeded to show how it could be done. Heisenberg also indicated the restrictive effect on the development of atomic theory of the endeavour to run together the idea of electron motion within an atom, subject to the usual kinematic ideas and regarded as a resultant of a simultaneously existing group of harmonically related components, with the physical fact of spectroscopic lines subject to a law of frequency so different to the law of a series of harmonic terms; so he surmised it would be wiser to cease to trouble ourselves about electron movements which never come into the actual field of observation. No doubt this would require a recasting of the

mathematical treatment and Heisenberg gave an indication of the way to proceed. Another feature of interest to the scientific historian is the fact that in both instances the pure mathematicians of the nineteenth century had actually, without any prevision of the use the physicists were destined to make of them, invented the suitable mathematical conceptions and developed and perfected the necessary technique ; the calculus of tensors and the calculus of matrices were both to hand when the right moment for their physical applications arrived, although to be strictly accurate in our statements, both Einstein and Heisenberg had to be informed of their good fortune by the mathematicians.

Naturally our subject, Statistical Mechanics, is being brought into line with the Quantum Mechanics of this new period. Just as naturally that is a matter outside the province of a book of this nature.* The author, however, begs his youthful readers not to be too downcast on that account. The kind of feeling that "classical and classical-quantum stuff" is dead and done with, and that it is just so much waste time to bother about it is very unjustified. We travel quickly in these days no doubt, but I doubt if any serious teacher of physical science can see how it would be possible to introduce the immature and youthful mind to the newer knowledge without an adequate training in the traditional conceptions, the manner in which they synthesised the older knowledge, and the manner in which they were modified and replaced by broader ideas. After all it was to deal with difficulties in statistical mechanics that "Quantum" was first invented, and nearly all the work of the first period was concerned with this purpose ; and as regards the second period, the conception of "stationary states" is still required in order to follow the generalisation to the new formulation of Quantum theory. As far as the matter of "seeing results as quickly as possible" is concerned (which we at the outset assumed to be the desire of the majority of readers), there is no need to be alarmed ; the first and second periods have provided them in abundance.

* Nevertheless, an Appendix at the end of the book will give the reader some idea of what has happened very recently.

14.2 Planck's Constant.—At the time of Planck's first suggestion with its flavour of "heterodoxy," one of the problems agitating the minds of the physicists was connected with the discrepancy between the facts of black body radiation as discovered by an improved technique in radiometric measurements and the theoretical laws as deduced from dynamical principles and the equations of the electromagnetic field. Thermodynamical reasoning carried the work far enough to recognise that the formula for the density of radiation in a uniform temperature enclosure has a certain general character ; * in it, however, there occurs an unknown functional form, unknown, *i.e.*, in the sense that thermodynamics alone can give us no information about it. For progress towards its discovery an appeal to electromagnetic and dynamical theory had to be made. Unfortunately, if that appeal was made in a strictly "lawful" way, the result was seriously at variance with the facts. Planck working hard at the problem on its theoretical side, gradually narrowed down the region in which the fallacious step was to be found. At last he put his finger on it ; it turned out to be the assumption of equipartition of energy on the average between co-ordinates and momenta in any molecular system *which contribute squared terms to the expression for the energy*. The italicised words are important. No doubt there is no equipartition if that condition is not satisfied, but Planck was using as a model radiating and absorbing mechanism the harmonic oscillator (the faithful ally of the mathematical physicist, which had never yet failed him), and its energy was a sum of squared terms. It availed nothing to point out that after all this was a very crude model of the radiating processes in an atom. The nature of the reasoning was such that any *conceivable* mechanism following dynamical laws should yield the proper result. But the law of equipartition of energy is derived from statistical-mechanical reasoning, and that is how our subject became mixed up with all the trials and tribulations of that period.

To appreciate Planck's hint as to how to escape from the

* Wien's Displacement Law.

dilemma, we will introduce the reader to his way of deriving the law of equipartition. His statistical reasoning in his first papers did not follow quite the same course as that employed in our earlier chapters, but as a matter of fact, his particular way of choosing complexions and counting them, has reappeared quite lately in the literature of the subject. Added to that, it has an interest of its own, and is, of course, quite sound; so it should be known to any one interested in the elements of the subject.

Planck conceived a given number of oscillators vibrating about fixed mean positions in an all-pervading reservoir of energy, viz., the field of full radiation. Between the field and the oscillators there was flux and reflux of energy. Just as in the beginning of our statistical reasoning we had to postulate *finite* phase-cells, which we afterwards reduced to mathematical infinitesimals, so he postulated *finite* elements of energy, each passing as it were, entire, and not continuously in small infinitesimal elements, at exchange between oscillator and field. Call each element η . Suppose that at any moment the n oscillators have between them c of these elements, so that their total energy is $c\eta$. How many ways can this be done? All the c elements might be in the first oscillator; represent this symbolically by a_1^c , or all in the second represented by a_2^c , and so on; or $c-1$ of them might be in the r^{th} and one in the s^{th} represented by $a_r^{c-1} a_s$, and so on. As all the elements of energy are supposed to be indistinguishable the number of ways of partitioning the energy E among the n oscillators is the number of terms in the expansion

$$(a_1 + a_2 + \dots + a_n)^c$$

and this is known to be

$$\frac{(n+c-1)!}{n! (c-1)!} \dots \dots \dots (14.2.1)$$

Now when in equilibrium with the radiation, the oscillators will have the temperature θ of the radiation, and possess a definite energy E . The whole system radiation and oscillators will then statistically be in its most probable

state. If there are N elements of energy altogether present, the total number of complexions in this state is

$$f(N - c) \frac{(n + c - 1)!}{n! (c - 1)!} \quad . \quad . \quad . \quad (14.2.2)$$

where $f(x)$ is the number of ways of distributing x elements of energy in the radiation, and $c = E/\eta$; for with any one way of distributing the $N - c$ elements in the temperature-enclosure, there can be combined one way of distributing c elements among the oscillators to yield one way of distributing all the N elements among the various parts of the whole system. As usual, we take the entropy of the system in this equilibrium state to be k times the logarithm of (14.2.2), together with a constant term which for our purpose may be ignored as it will disappear in the differentiation to be carried out presently. It is plausible to regard the two parts into which this expression falls as the entropy of the radiation and the entropy of the oscillators respectively. So if S is the entropy of the oscillators

$$\begin{aligned} S &= k \log \frac{(n + c - 1)!}{n! (c - 1)!} \\ &= k \log \frac{(n + c)!}{n! c!} \quad * \\ &= k(n + c) \log(n + c) - k c \log c - k n \log n. \end{aligned}$$

If the temperature of the enclosure be altered to $\theta + \delta\theta$, the energy of the oscillator system will be altered to $E + \delta E$ and its entropy to $S + \delta S$, and we know from thermodynamical reasoning that as no external work is done

$$\frac{\delta S}{\delta E} = \frac{1}{\theta}$$

in the limit. But $\delta E = \eta \delta c$. Hence

$$\begin{aligned} \frac{1}{\theta} &= \frac{1}{\eta} \frac{dS}{dc} \\ &= \frac{k}{\eta} (1 + \log \frac{n + c}{n} - 1 - \log c) \end{aligned}$$

* We are assuming that the elements of energy are much more numerous than the oscillators so that $(n + c)/c$ is practically unity.

$$= \frac{k}{\eta} \log \frac{n+c}{c}.$$

$$\text{Thus } \frac{n}{c} = e^{\eta/k\theta} - 1,$$

$$\text{or } \frac{E}{n} = \frac{\eta}{e^{\eta/k\theta} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14.2.2)$$

This reasoning may seem extremely abstract to the reader, who may be pardoned if he feels that the radiation is a very shadowy kind of material to partition elements of energy among; nothing so tangible for example, as the "solid" particles of our earlier "games of chance." It would not be so to any one imbued with present-day ideas of the essential "substantiality" of the radiation, in so far as it possesses all the so-called mechanical properties of matter, mass and momentum, as well as energy. Be that as it may, he may feel reassured when he learns that the result (14.2.2) for the average energy of an oscillator is equipartition of energy, if we just carry the analogy with our former procedure to its logical limit, *viz.*, assume that the elements η are mathematical infinitesimals, as we formerly assumed the phase-cells, in terms of which we defined complexions and states, to be infinitesimals in our final calculations. If we do so, the right-hand side of (14.2.2) is equal to

$$\frac{\eta}{\eta/k\theta + \frac{1}{2}(\eta/k\theta)^2 + \frac{1}{6}(\eta/k\theta)^3 + \dots}$$

which approaches the value $k\theta$ as η approaches zero. And so the average energy of the oscillator becomes $k\theta$, and this agrees with our former result, $\frac{1}{2} k\theta$ of kinetic, and $\frac{1}{2} k\theta$ of potential on the average.

However, it was the really brilliant idea of Planck just to refuse to go to the limit. With a flash of insight he saw that in refusing to do so, and in thus denying the equipartition law (as we shall see presently) lay salvation. Here we must take on faith a result which concerns the electrodynamical side of Planck's complete argument as distinct from the purely statistical with which we have been immediately

concerned. In that he had deduced the relation between the energy-density of the radiation and the average energy of an oscillator in temperature equilibrium with it. If he took the latter to be $k\theta$, the result was at variance with experiment; so he took (14.2.2) as it stands with η finite, and considered the conclusion to be drawn from that. At once he saw that in order to satisfy the general character of the formula for the energy-density, derived from purely thermodynamical reasoning and referred to on page 130, η would have to be proportional to the frequency of the oscillator and the constant of proportionality would, moreover, be a universal constant. So calling the frequency ν he wrote

$$\eta = h\nu,$$

and so

$$\frac{E}{n} = \frac{h\nu}{\exp(h\nu/k\theta) - 1} \quad . \quad . \quad . \quad (14.2.3)$$

From this could be derived at once a formula for the energy of full radiation as distributed among its various frequencies. Within a short time the experimental physicists were convinced that it was correct, and derived from the observations a value for h which has since been confirmed in several experimental researches inspired by other applications of the quantum idea. The accepted value for h is

$$6.55 \times 10^{-27} \text{ erg-seconds,}$$

for, as will appear at once, its physical dimensions are the product of energy and time, *i.e.*, the dimensions of action.

14.3 The “Quantised Paths” of an Oscillator.—We have given Planck’s original treatment (somewhat amplified) of the statistical side of the problem. It will be interesting to deal with the matter in a manner more in keeping with the methods which we have used hitherto, now that we appreciate Planck’s break with tradition. This will have the added advantage that it will give us also a truer idea of where the “quantisation” is really situated. In terms of the conceptions of section (14.2) we naturally speak of “quanta of energy,” but if there is any idea latent in the reader’s mind that this *must* imply discrete “atoms” of

energy preserving an identity through all vicissitudes, as we have been accustomed to assume for atoms of matter, he must disabuse his mind at once of this idea. Planck himself would have none of it in those days and when Einstein, in his study of the photoelectric effect, propounded quantum views savouring very much of such heretical notions, Planck protested vigorously, and recast his whole presentation in such a manner as to bar out this idea, which was really at that time repugnant to the sense of continuity produced by the theory and the experimental facts of the propagation of radiation. No doubt the oscillator could only take in "lumps" of energy, $h\nu$, or get rid of them if it emitted or absorbed at all. The reader will realise that the whole of the argument would be upset, if there could be *fractions* of η in an oscillator as well as integral multiples. But once out, the energy merged into the continuous field. Nevertheless, one conclusion could not be avoided; between emissions and absorptions the vibrations of the oscillator could only be executed with one of a discrete series of amplitudes; *i.e.*, it could only exist in one of a discrete set of "quantum states." We are familiar in ordinary mechanical reasoning with the notion that a harmonic vibrator can be given any of the infinite number of amplitudes between zero and some upper limit. But that notion will not serve here. We can very readily select those "quantised" amplitudes, by means of the information already obtained.

In the symbolism of section (5.1) the energy of the oscillator is

$$\frac{1}{2} a \dot{q}^2 + \frac{1}{2} b q^2$$

or

$$\frac{p^2}{2a} + \frac{bq^2}{2}.$$

If this has a constant value, ϵ , the representative point of the oscillator in a phase-diagram will be on the ellipse

$$\frac{q^2}{2\epsilon/b} + \frac{p^2}{2\epsilon a} = 1.$$

Its semi-axes are $(2\epsilon/b)^{\frac{1}{2}}$ and $(2\epsilon a)^{\frac{1}{2}}$, and its area is the product of these by π , *i.e.*, $2\pi\epsilon(a/b)^{\frac{1}{2}}$.

But $(b/a)^{\frac{1}{2}}$ is the pulsance, $2\pi\nu$, of the vibration, and so the area of the ellipse is

$$\frac{\epsilon}{\nu} \quad . \quad . \quad . \quad . \quad . \quad (14.3.1)$$

In consequence, if in this quantum state the oscillator holds r "quanta of energy of frequency ν ," its elliptical phase-path has the area

$$r h \quad . \quad . \quad . \quad . \quad . \quad (14.3.2)$$

Thus the discrete quantum paths of the representative point in the phase-diagram of the oscillator are a series of similar ellipses separated from each other by elliptic annuli of area h , the lowest quantum condition being represented by the origin. Thus no matter what the value of ν is, *i.e.*, no matter what is the value of the quantum of energy, the phase-diagram is divided up into areas always of the same magnitude. The only quantum which has so far any claim to atomicity is thus the "quantum of action," for it is action which is represented by an area in the phase-diagram. It will be wise to remember that a quantum state is not a static condition; the oscillator vibrates to and fro, and the representative point keeps rushing round the appropriate ellipse between the "catastrophic" emissions and absorptions.

The statistical problem is now easily dealt with in our more customary manner. A complexion of the system of oscillators is determined by the manner in which we assign individual, identifiable points to the various ellipses; there will be some outer limit settled by the whole energy of the system. The ellipses take the place of the phase-cells in our previous arguments; an interchange of points between ellipses alters the complexion, but not the statistical state; * a mere shifting of points along the ellipses does neither. The number of ways of assigning n_0 points to the origin, n_1 to the first ellipse, n_2 to the second, and so on, is

$$\frac{n!}{n_0! n_1! n_2! \dots}$$

* Do not confuse the two uses of the word "state" from this point onward. We speak of a "quantum state" of an oscillator, and, later, of an atom; "Statistical state" still refers to the whole system of oscillators or atoms.

We then proceed as before. The logarithm of this is varied and the variation put equal to zero. The conditions for constant total number and total energy introduced, and we arrive at the usual result. In the most probable state the number of oscillators in the r^{th} quantum state is

$$C e^{-\mu \epsilon_r}$$

where

$$\epsilon_r = r h \nu.$$

The constant μ is, as usual, identified with $(k\theta)^{-1}$; for we are really considering the oscillators now as denizens of gas atoms in the manner of Chapter V.

To determine C , we have

$$\begin{aligned} C (1 + e^{-\mu h \nu} + e^{-2\mu h \nu} + e^{-3\mu h \nu} + \dots) &= n^* \\ \text{or} \quad C &= n (1 - e^{-\mu h \nu}) \quad (14.3.3) \end{aligned}$$

The whole energy in the oscillators is

$$C \sum_{r=0}^{\infty} \epsilon_r e^{-\mu \epsilon_r}$$

which is equal to

$$\begin{aligned} & C h \nu (e^{-\mu h \nu} + 2 e^{-2\mu h \nu} + 3 e^{-3\mu h \nu} + \dots) \\ &= n h \nu (1 - e^{-\mu h \nu}) e^{-\mu h \nu} (1 + 2 e^{-\mu h \nu} + 3 e^{-2\mu h \nu} + \dots) \\ &= \frac{n h \nu (1 - e^{-\mu h \nu})}{(1 - e^{-\mu h \nu})^2} e^{-\mu h \nu} \\ &= \frac{n h \nu}{e^{\mu h \nu} - 1}, \end{aligned}$$

or the average energy of an oscillator is

$$\frac{h \nu}{e^{\mu h \nu} - 1},$$

as before.

It will be seen that in the most probable statistical state of the system, the majority of the oscillators are in the lowest quantum state represented by the origin, the number in the next quantum state is obtained by multiplying the former

* The unity in the series arises from the lowest quantum state, $r = 0$.

by $\exp(-h\nu/k\theta)$, in the next by $\exp(-2h\nu/k\theta)$, and so on. If the temperature θ decreases the multiplier $e^{-\mu h\nu}$, becomes smaller and smaller approaching zero as θ approaches zero. Thus as the temperature falls, the oscillators tend to crowd into the state of zero energy. If θ , on the other hand, increases, the exponential factor increases gradually having unity as its limit when θ is infinite. Thus there is with rising temperature a tendency towards more equal distribution of the oscillators among the quantum states.

14.4 Planck's Alternative to the Strict Conception of Quantum States.—It is possible that the reader may not quite realise the point of the extreme hostility to Planck's views at the time. The assumption of quantum states seems harmless enough in its way, and the statistical argument, at all events in the form outlined in section (14.3), appears as unimpeachable as it was in earlier applications. That is true enough; it was not the statistical part of his investigation which failed to command general assent at first. But there was another part just as necessary to the argument, and in that part Planck assumed that the amplitude of the oscillator could vary in a continuous manner. The oscillator is subject to the electromagnetic forces in the radiation and those forces which have the same frequency as the oscillator, or frequencies relatively near, impress an oscillation of increasing amplitude on it—an illustration of the well-known phenomenon of resonance. The safeguard against undue heaping up of energy in the oscillator is its own radiation due to the accelerated motion which its vibration implies. The balance between absorption and radiation is required to keep it in an average condition as regards energy, whether that condition be equipartition or any other. The mathematical equation which expresses that balance leads to the relation between the density of each constituent of full radiation and the average energy of oscillators with the corresponding frequency. Thus it will be seen that this side of the argument was absolutely essential to Planck's final result, and in working it out he had to assume the continuous increase or decrease of the energy in the oscillator. In an endeavour to minimise the

contradiction as far as possible, and as a protest against what he considered to be an unnecessary extension of his idea, he recast the statistical argument so as to suit at all events the assumption of continuous absorption, although he still had to keep discontinuous emission in it. Though it has not much place in the general exposition of quantum physics, as it developed later, it should be known to the student of these matters, as it suggests one conclusion which may possibly be justified soon as an experimental fact. To appreciate its point of difference with the first method, let us conceive that the phase-diagram is partitioned into phase-cells by drawing equal energy ellipses very near to one another. The phase-cells are the elliptic annuli, each of area $\delta\epsilon/\nu$ where $\delta\epsilon$ is the step of energy between one ellipse and the next. By classical methods the density of points in an annulus is proportional to $e^{-\mu\epsilon}$ and the number in it is $D e^{-\mu\epsilon} \delta\epsilon/\nu$ where D is a constant given by

$$\frac{D}{\nu} \int_0^{\infty} e^{-\mu\epsilon} d\epsilon = n \quad . \quad . \quad . \quad (14.4.1)$$

so that $D = n\nu\nu$. In obtaining this, we have, as formerly, narrowed down the cells to infinitesimal dimensions in the last resort. In the equilibrium state as many representative points pass outward in a given time across any given ellipse (absorption) as pass inward across it (emission), and an inward, or outward journey could start from any point. But in Planck's second form of his theory, an inward journey could not start from any point; once a representative point has passed out beyond one of the critical ellipses of area h , $2h$, $3h$, etc., it cannot move inward; not until it has reached the next critical ellipse is that possible. In short, emission is only possible at certain critical amplitudes. At such critical moments of its history the oscillator *may* radiate or it may pass on into the next "zone of safety" free to gather up energy for another spell without danger of loss. But some of the oscillators are bound to radiate when they reach any critical ellipse; otherwise the balance between absorption and emission over relatively long periods would not be maintained. When one speaks of an "outward

journey," one visualises the representative point on the phase diagram executing a spiral path gradually widening out from the origin; such a path may terminate suddenly at the first critical ellipse and restart at once from the origin, or it may continue widening out uniformly in the annulus between the first and second ellipses until it reaches the latter, when it may still continue or suddenly stop and make a fresh start from the origin; and so on. Thus the number of points in any h annulus is at any moment less than in the one just inside it and more than in the one just outside; but just how much less and how much more? Well, one can, as before, consider these h annuli as *finite* cells, and assign n_1 points to the first, n_2 to the second, and so on, and proceed to work out the most probable state; but in writing down the constant energy condition we realise that all the points in one of these cells do not correspond to the same energy; we cannot assume that, as we are not ultimately going to make these cells infinitesimal in size. A plausible proposition is that the points in an h annulus are uniformly distributed over it, and in that case when we write the equation

$$\Sigma n_r \epsilon_r = E,$$

ϵ_r is the mean energy of the r^{th} annulus, *i.e.*, it is equal to $(r - \frac{1}{2}) h\nu$. The usual result emerges

$$n_r = C e^{-\mu \epsilon_r}$$

where

$$\epsilon_r = (r - \frac{1}{2}) h\nu.$$

As usual C is determined by

$$C \sum_{r=1}^{\infty} e^{-\mu \epsilon_r} = n,$$

or

$$C e^{-\frac{x}{2}} (1 + e^{-x} + e^{-2x} + \dots) = n,$$

where x is for the moment written instead of $\mu h\nu$.

Thus

$$C = n e^{\frac{x}{2}} (1 - e^{-x}).$$

The whole energy E is given by

$$\begin{aligned}
 E &= C \sum_{r=1}^{\infty} \epsilon_r e^{-\mu \epsilon_r} \\
 &= C \frac{h\nu}{2} \left\{ e^{-\frac{x}{2}} + 3 e^{-\frac{3x}{2}} + 5 e^{-\frac{5x}{2}} + \dots \right\} \\
 &= \frac{nh\nu}{2} (1 - e^{-x}) \left\{ (1 + e^{-x} + e^{-2x} + \dots) \right. \\
 &\quad \left. + 2(e^{-x} + 2e^{-2x} + 3e^{-3x} + \dots) \right\} \\
 &= \frac{nh\nu}{2} + nh\nu (1 - e^{-x}) \frac{e^{-x}}{(1 - e^{-x})^2} \\
 &= \frac{nh\nu}{2} + \frac{nh\nu}{e^x - 1}.
 \end{aligned}$$

Thus the average energy of an oscillator is now

$$\frac{h\nu}{\exp(h\nu/k\theta) - 1} + \frac{h\nu}{2} \quad . \quad . \quad . \quad (14.4.2)$$

There is an interesting difference between this result and (14.2.3). If we make θ gradually approach zero, the expression (14.4.2) does not approach zero but $h\nu/2$ as its limits; thus at absolute zero the system of oscillators would have an energy of amount $nh\nu/2$. Planck could still make this new expression yield the satisfactory expression for black body radiation, and he was also able to use the new model in an explanation of the (then) puzzling features of the photo-electric effect without recourse to Einstein's light-quanta. This being so, he felt justified in asserting that here there was theoretical evidence of the possibility that at absolute zero of temperature matter is not quite devoid of energy. The existence of "nul-point energy" is suggested.

The number of oscillators in one of the finite energy ranges defined by the critical states of emission bears to the number in the range just below the ratio e^{-x} to unity. Thus the chance that an oscillator will radiate when it reaches a critical state is $1 - e^{-x}$, provided it radiates the whole amount which it contains and restarts a fresh accumulation of energy from that condition. In his statistical-electrodynamic argument, Planck assumes that emission has this

character, and introduces a definite postulate about the chance of emission in a critical state; these hypotheses correspond to the assumption made above in this simplification of his argument, that the points in an h annulus are equally distributed. The reader will observe that in his first exposition emission had not of necessity this character; the representative point could jump about from ellipse to ellipse, in its changes of state, inward or outward; if inward, the leap was not necessarily right to the origin.

CHAPTER XV

THE THEORY OF THE STATIONARY STATES OF AN ATOM

15.1 The “ Action-Integrals ” of a System.—Notwithstanding Planck’s conservative tendencies the movement which he initiated took his first idea as its guide for further development. To see how this came to pass, we must deal with some general dynamical features of more complex systems than a simple harmonic oscillator ; it is too crude a model for further exposition. For one thing the assumption that even for an oscillator with but one degree of freedom the period is independent of the amplitude, is not really true of the many physical systems which the oscillator is taken to represent in elementary statements—the pendulum for instance, or the body bobbing up and down at the end of a spring. But if this is so, the apparent simplicity of quantising by means of the energy content disappears, as that clearly depends on a constant frequency. But we saw that another way of declaring how to select the quantum states of the harmonic oscillator is to say that the choice will fall upon those amplitudes for which the accumulated action in one period is once, twice, thrice, etc. the value h . This choice is still open to us, and during the second period, referred to in section 14 . 1, it was the keynote to the whole situation.

The restoring force which controls the oscillator not being proportional to displacement beyond minute values of the latter, it turns out, as stated, that the frequency of the oscillation depends on the amplitude. The oscillator will, however, in any actual vibration, have a definite momentum, p , for a given value of displacement, q . (It must be clearly understood that “ damping ” is excluded from consideration.) The integral of $p dq$ can be calculated from the knowledge of the particular law of force, and if this integral is calculated

for the complete period which exists for this given vibration, we shall denote its value by J . This accumulated action in one period is usually termed the "action-integral" of the system. It is like an integration constant occurring in the statement of q as a function of the time; it is a "constant" during any movement involving a given amplitude, but varies in value if the swings are altered so as to involve a wider or narrower range. Amplitude, frequency and energy can all be expressed as functions of J . It will be recalled that in the case of a harmonic oscillator, if the energy of a particular vibration is ϵ , then the accumulated action in one period is ϵ/ν , so that the quotient of the former by the latter is the frequency, or to put it another way, any finite change in the energy if divided by the change in the action-integral accompanying it, gives the frequency of oscillation. The result for an "anharmonic" oscillator is a generalised form of this. Let $E(J)$ be the function of J , which is equal to the energy; $E(J + \delta J)$ is equal to the energy for a slightly different amplitude with an action variable $J + \delta J$. It can be proved that on dividing $E(J + \delta J) - E(J)$ by δJ and going to the limit, we obtain the frequency of the oscillation with the action-integral J . In short, the frequency of oscillation is $dE(J)/dJ$. In addition to this modification of the results it must be borne in mind as well that we cannot write

$$q = A \cos (\omega t - \epsilon)$$

where

$$\omega = 2 \pi \frac{d E(J)}{d J}.$$

The oscillation is not a *simple* harmonic one. Instead it is known that the correct result is

$$q = A_1 \cos (\omega t - \phi_1) + A_2 \cos (2 \omega t - \phi_2) + A_3 \cos (3 \omega t - \phi_3) + \dots$$

where $\phi_1, \phi_2, \phi_3, \dots$, the epoch-angles, and A_1, A_2, A_3, \dots are known functions of a second integration constant and J .* The selection of the quantised oscillations for this

* The equation of motion is of the second degree, and in its complete solution *two* integration constants must make their appearance.

oscillator is, if we adopt the method used for the model atoms of Bohr's theory, made by choosing those whose action-integrals are whole-number multiples of h . To be strictly accurate it was discovered as time went on that some experimental results were more easily brought within the bounds of the theory if this selection were interpreted a little more loosely and "half-quantum numbers" allowed, so that the action-integrals might be put equal to rJ or $(r + \frac{1}{2})J$ where r is a positive integer. As a matter of interest this extension of the quantising principle does for certain systems emerge quite naturally from the most recent formulation of Quantum mechanics. It should, however, be noted carefully that this extension does not bring in its wake any necessity for "half-quanta of energy." The reason why will appear presently.

To go on to a system with two degrees of freedom, such as the ordinary pendulum might be considered to be, an interesting feature of the vibrations of such a system can be observed very readily by giving a pendulum a slightly elliptical swing. It soon appears that the orbit of the bob is not an ellipse, nor indeed any *closed* oval curve. Roughly we say that the plane of vibration of the string is rotating round. Strictly, of course, there is no such plane. Another mode of expression is to say that the bob is going round an elongated ellipse, whose long axis is slowly "precessing" in a horizontal plane in the same sense as the motion of the bob round the orbit. What is really happening is that the bob does not return to the same place at its places of greatest and least distance from the centre. This arises from the fact that it has really two *distinct* periods of vibration, which may be nearly equal but are not exactly so. The amplitude one way is quite large; at right angles to that way quite small. It will happen, of course, that if the two periods have values which are commensurable then ultimately the curve after many convolutions will "re-enter" into "itself," and the body proceed to execute the same path once more. But if the periods are incommensurable, this is not so. The simplest way of bringing out the two periods is to realise that there is a certain interval during which the radius

vector from the centre changes from its greatest value to its least, then to its greatest, once more to its least, and finally to its greatest. This is one period, the period of "libration" of its radius vector. (We are really at the moment thinking of a vibration truly in a horizontal plane; actually the bob of a pendulum travels on a spherical surface.) On the other hand, the angle which this radius vector sweeps out in the horizontal plane, increases by 2π in a different time; in this time $\cos \theta$ and $\sin \theta$, where θ is this "azimuthal" angle, librate in value between the maximum and minimum values, $+1$ and -1 , and back again. In this system the accumulation of the action goes on in two ways. The vibrating body has a certain angular momentum round the origin, $mr^2\dot{\theta}$, where r is the radius-vector to its position on the oval path; if we integrate $mr^2\dot{\theta}d\theta$ between 0 and 2π , we obtain one action-integral J_1 . The body also has a linear momentum $m\dot{r}$ to and from the origin; if we integrate $m\dot{r}dr$ throughout the period of radial libration, we obtain a second action-integral J_2 . The energy in any prescribed orbit can be found from a knowledge of its two action-integrals; if $E(J_1, J_2)$ is the function which is equal to the energy, then the two frequencies azimuthal and radial are

$$\frac{\partial E(J_1, J_2)}{\partial J_1} \quad \text{and} \quad \frac{\partial E(J_1, J_2)}{\partial J_2}$$

respectively. That is known from dynamical theory. The expressions for r and θ in terms of t take the form

$$r = \sum_{r=-\infty}^{\infty} \sum_{s=-\infty}^{\infty} A_{rs} \cos \left\{ (r\omega_1 + s\omega_2) t + \phi_{rs} \right\}$$

$$\theta = \sum_{r=-\infty}^{\infty} \sum_{s=-\infty}^{\infty} B_{rs} \cos \left\{ (r\omega_1 + s\omega_2) t + \phi_{rs} \right\}.$$

Here the A_{rs} , B_{rs} and ϕ_{rs} are functions of J_1 , J_2 and two other integration constants, and as stated, $\omega_1 = 2\pi \partial E / \partial J_1$, $\omega_2 = 2\pi \partial E / \partial J_2$.

We have here an example of a "conditionally-periodic" system. The system may not apparently be periodic; for we have seen that if ω_1 and ω_2 are incommensurable, the

vibrating body never really returns to any former position, but the solution shows how the periodicity is latent in artificially separated parts of the motion.

The suggestions for quantising in this case follow the same lines as before ; the quantised paths are chosen so that $J_1 = r_1 h$ and $J_2 = r_2 h$ where r_1 and r_2 are positive integers (or numbers such as $r + \frac{1}{2}$ may be involved).

15.2 Bohr's Postulates for the Atom.—Possibly the reader may now begin to have some idea of the quantisation of orbits, and how action and Planck's h constant are involved in it. Taking the hydrogen atom with its single electron, it has to be observed that the strictly elliptic orbit of the electron round the nucleus as a focus, deduced from the simple inverse square law of attraction, is too ideal. Owing to a variety of causes, the forces caused by neighbouring atoms, or external fields imposed by an experimenter in the study of the Zeeman and Stark effects, or the relativity change of mass in the electron due to changing speed in the orbit, the orbit is not really re-entrant. Just as we have pointed out in the case of the two-dimensional anharmonic oscillator, there are two periods, one involved in the libration of the radius vector between its extreme values, one in the increase of the azimuthal angle by 2π , and a repetition in the values of its circular functions. Two action-integrals are involved just as before, and one of Bohr's fundamental postulates consisted in assuming that, despite the deductions of classical dynamics, the orbits whose action-integrals are equal to integral multiples of h have an inherent stability, non-dynamical to be sure, but physical in the sense that the assumption could be used with great effect to unravel for the first time some of the intricacies of spectroscopic observations which had hitherto baffled physicists. The remaining non-quantised paths, just as dynamical and from the point of view of Dynamics just as "unstable" as the quantised, are irrelevant to the explanation of the physical facts. Conceivably, if undisturbed, the electron could remain in a quantised orbit for ever, but if disturbed, it would have to find a new semi-permanent home in another quantised orbit, not in any of the mechanically possible, but "quantically"

impossible orbits. The atom has a discrete number of "stationary states."* It should be mentioned that Sommerfield and Schwarzschild gave considerable assistance at the outset on the mathematical side in applying the quantising rules to particular problems.

The second postulate of Bohr concerns the "quantum-jumps" during which the atom leaves one stationary state and enters another. In Planck's early oscillator theory the quantum of energy is determined by the frequency of the oscillator vibration; h if multiplied by the latter gives the former. In view of the multiplicity of *kinematic* frequencies now involved, no success in that direction seems possible. Bohr's ingenious modification lay in *dividing* the change of energy between two states by h to obtain the frequency of the emitted or absorbed radiation. Optical frequencies ceased to be identified with kinematic. Terra firma began to appear in the region of spectroscopy where, in the word of the late Lord Rayleigh, there had been formerly a "bog."

We have assumed that the orbit of the electron is in one plane; virtually that limits the degrees of freedom to two; two co-ordinates are sufficient to determine the position of the electron; there are two distinct action-integrals for any orbit, classical or quantum, and in consequence two fundamental frequencies involved in each orbit. But the degrees of freedom are really three; our limitation of the orbit to one plane has concealed that fact. But if we apply some external force to the electron, such as a magnetic field, the normal to the plane of the orbit precesses round a line through the nucleus parallel to the field, just as the axis of a spinning top precesses round the vertical. To define the electron completely now we must have a co-ordinate defining the plane of the orbit or the normal to it, in addition to the radius vector and azimuth of the electron in the orbit. This can be chosen to be the angle made by a plane containing the normal to the orbital plane and the field line through the nucleus with any reference plane containing the latter line. This precession involves additional energy; and also

* Note that "stationary" does not mean "static." There is plenty of movement in a stationary state.

a new angular momentum round the field line. From the latter, using dynamical laws, can be calculated a third action-integral equal to the amount of action accumulated in this fashion in the period of precession, the third period of the system. Classically this may have any value; the requirements of the Quantum hypothesis limit it again to integral multiples of h . This amounts to stating that the orbit can only have a set of discrete orientations with respect to the external influence. Hence arises "space-quantisation," and a third quantum number enters in the selection of stationary states.

Nor is this all. In our solar system the planets spin on their axes as well as rotating round the sun in their orbits. So in recent years the "spinning electron" has come along to give us a hand in this entertaining puzzle of defining stationary states so as to conform to the spectroscopic, the magneto-optic, the electro-optic and the thermal evidence. This involves another angular momentum and period; another action-integral and a fourth quantum number.

All this has been written in connection with the single-electron atom. As a matter of fact, in view of a special feature of Bohr's theory of optical spectra, it holds good in an approximate way for much more complicated atoms. Further we can hardly go without transcending the limits of space and possibly the reader's ability to follow the necessary analytical statements. In the last resort, if there are l electrons, we can (regarding the nucleus as sufficiently massive) think of the system as having $3l$ degrees of freedom. The radial vectors of the electrons will librate between maximum and minimum values, the angles necessary for co-ordination will also librate or their circular functions will. These are necessary conditions of periodicity and stability, even if they are not sufficient. The whole theory can be worked out under certain definite mathematical assumptions. There are $3l$ action-integrals involved, and $3l$ frequencies given by the same rule as before

$$\nu_r = \frac{\partial E(J_1, J_2, \dots, J_{3l})}{\partial J_r}.$$

Quantisation chooses those states of orbital motion in which the J_z are whole-number multiples of \hbar , and so each stationary state corresponds to a definite set of $3l$ integers. In fact, in recent theory less and less interest is being shown in the attempt to make pictures of the orbits or give analytical expressions for them. The state is determined by its quantum numbers. If we know the energy as a function of the quantum numbers, *i.e.*, of the action-integrals, the change of energy in a jump from one state to another can be calculated, and the frequency of the emitted radiation obtained by Bohr's second postulate. The results must, of course, agree with spectroscopic evidence ; that acts as a check on any hypotheses we introduce for formulating the energy in terms of the quantum numbers. For that purpose the model atoms of the older period with their electron orbits have still their uses, but the clear cut planetary picture seems at the moment to have the same doom confronting it as the ether—not so much actual denial as mere apathy. Useful, perhaps, as mental helps for those without the necessary mathematics, but beyond that of little use.

CHAPTER XVI

DISTRIBUTION OF A SYSTEM IN ENERGY

16.1 Quantisation and *à priori* Probability.—When dealing with complexions and statistical states of a molecular system, we introduced as a fundamental hypothesis the statement that all complexions have the same *à priori* probability which involves in its turn the assumption that the representative point of a given molecule is as likely to be in one phase-cell as another. That of necessity implies that the phase-cells have all the same magnitude. Similarly in dealing with Planck's oscillator and deriving his expression for the average energy in section (14.3), we obviously assumed that an oscillator is as likely to be on one quantum path as another; these paths take the place of the equal-sized phase-cells in the classical treatment of non-quantised systems, and again all complexions have the same *à priori* probability. So long as a system does not involve both quantised and non-quantised elements, no necessity to fit the two aspects together arises; nor is it even troublesome to deal with a system of complex molecules whose positions and translatory movements follow classical laws and whose internal oscillations follow quantum laws.

But suppose we have to deal with the ejection of electrons from atoms in the photo-electric effect or ionisation caused by collisions or X-rays; or dissociation where atoms are at times bound as parts of larger particles and at times are free and independent particles themselves; or sublimation of molecules from a solid state. In these examples we see the possibility of a system being composed of particles any one of which may be in a quantised path sometimes and in a non-quantised path at other times. In the latter condition, division of a phase-diagram into phase-cells is the suitable machinery for counting complexions; in the former not so;

quantum paths must be used. How are we to combine the two ideas ? Even if we regard all quantum paths as equally likely between themselves, and all phase-cells as equally likely among themselves (*i.e.*, that a particle is as likely to be in one phase-cell as in another if it is behaving in a non-quantum way, and on one quantum path as another if behaving in a quantum way), what is the chance that a particle will be in a given phase-cell as against the chance that it will be a given quantum path ? Clearly the answer will depend on the size of the cell ; the smaller it is the less the relative chance. The following procedure has been adopted on the grounds of its plausibility, and no facts are known with which it is at variance. Recalling as a simple illustration the case of Planck's oscillator, we see that a given quantum path concentrates on itself as it were, all the representative points which in classical conditions would be dotted about in the elliptical annulus between it and the next path or rather in the adjacent halves of the two neighbouring annuli which it separates. This area, whose points are thus swept into one linear channel, is h . Now if s is the area of a phase-cell, and S the area of the whole phase-diagram determined by the volume and total energy of the whole system of oscillators, then the *à priori* probability that a representative point, if classical motion were involved, would be in a given phase-cell, would be s/S . So it seems plausible to assume that the *à priori* probability that a representative point shall be on a given quantum path is h/S . Thus the relative probabilities for non-quantum and quantum possibilities is s/h , or, if we wish to avoid bringing in *à priori* probabilities explicitly, and content ourselves as hitherto, by counting complexions and making the number stand for the relative probability of a statistical state, we must assume that s is equal to h , *i.e.*, choose the phase-cells suitable for complexion-counting in non-quantised motions to have the size h .

This is for a system whose particles have one degree of freedom and whose phase-diagram is partitioned into areas which represent action. For a system whose particles have the usual three degrees of motion, it is a natural generalisa-

tion to take as the size of a phase-cell for non-quantised motions h^3 , and then to regard the representative point of a given particle to have the same *à priori* probability of being in non-quantised motion in a given phase-cell as of being in quantised motion on a given quantised path. Alternatively, if p is the *à priori* probability of the point being in six-dimensional phase-cell of size s , the *à priori* probability that it is on any quantised path is $p h^3/s$. Will the reader please bear in mind that in this we have not been considering the particles as having internal degrees of freedom themselves? They have been regarded as simple structureless particles capable of flying about in certain parts of the enclosure, just like the constituents of a gas, or, on the other hand, being "bound" to some centres of attraction, in other parts, and so probably subject to quantum conditions. The question of complex molecules does not involve so seriously the doubt we have referred to. The phase-diagram will then have a higher dimensionality than six; those extra dimensions which are required to deal with internal motions will, as far as we can judge, involve quantum methods throughout. There is a difference between the simultaneous existence of quantum conditions and non-quantum conditions for different degrees of freedom, and the alternation of the same degrees of freedom between periods of quantum motion and periods of non-quantum motion.

16.2 Energy-Hypersurfaces and Energy-Shells in the Phase Diagram.—In dealing with the structureless particles of the previous section, nothing has been said as regards the "shape" of the phase-cells. In earlier chapters it has been understood that the cell is analogous to a rectangle in a two-dimensional phase-diagram; *i.e.*, it is looked upon as an extension-in-phase, such that the co-ordinates and momenta corresponding to any phase in it are respectively greater than some set of values $x, y, z, \xi, \eta, \zeta$, and respectively less than $x + \delta x, \dots, \zeta + \delta \zeta$, where $\delta x, \dots, \delta \zeta$ are small increments. But there is no compulsion to adopt this view. The fact that in the most probable state the numbers in each cell involve e^{-u} as a factor suggests an alternative method of delimiting the cells which will prove convenient

at times. The energy of a particle is given by the function $(\xi^2 + \eta^2 + \zeta^2)/2m$, at all events in the absence of an external field (and ignoring also for the moment any internal energy or energy of rotation). All phases whose energies are individually less than ϵ are bounded by a region in the phase-diagram, such that

$$\xi^2 + \eta^2 + \zeta^2 = 2 m \epsilon \quad . \quad . \quad . \quad (16.2.1)$$

Its six-dimensional magnitude is determined by integrating $dx dy dz d\xi d\eta d\zeta$ throughout the volume of the system of particles as regards x, y, z , and throughout a sphere determined by (16.2.1) as regards ξ, η, ζ . The result is

$$\frac{4\pi}{3} (2 m \epsilon)^{\frac{3}{2}} v \quad . \quad . \quad . \quad (16.2.2)$$

where v is the volume of the system. The phases which satisfy (16.2.1) exactly, have a certain extension-in-phase, but it should be realised that it has not the full dimensionality (six) of the phase-diagram. Just as in ordinary geometry, the points whose co-ordinates satisfy an equation such as

$$f(x, y, z) = c,$$

have an extension which is only superficial, and do not occupy a three-dimensional volume, so the extension of the phases satisfying (16.2.1) is only five-dimensional. We call (16.2.1) a "hypersurface."* Apart from names, however, we realise that on strictly classical lines the chance that the phase of any particle in the system satisfies (16.2.1) is zero. But if we consider another hypersurface

$$\xi^2 + \eta^2 + \zeta^2 = 2 m (\epsilon + \delta\epsilon) \quad . \quad . \quad (16.2.3)$$

the phases which satisfy any equation

$$\xi^2 + \eta^2 + \zeta^2 = c,$$

where c has any value between $2 m \epsilon$ and $2 m (\epsilon + \delta\epsilon)$ occupy a six-dimensional region in the phase-diagram, and

* Of course (16.2.1) would represent an ordinary surface in a simple three-dimensional momentum-diagram. In the phase-diagram, however, six dimensions are involved. The absence of x, y, z in (16.2.1) shows that the hypersurface has "cylindrical" properties.

the chance of a particle in the system having one of these values is not zero; it is proportional to the size of this "energy-shell lying between" the hypersurfaces (16.2.1) and (16.2.3). The picturesque phrase "lying between" has a convenient brevity; its meaning is quite definite, and can be expressed analytically as above. The size of this shell can be obtained as the differential of (16.2.2); it is

$$2 \pi (2m)^{\frac{1}{2}} v \epsilon^{\frac{1}{2}} \delta \epsilon \quad . \quad . \quad . \quad . \quad (16.2.4)$$

Shells such as these lying between adjacent members of the family of hypersurfaces (16.2.1) for varying values of ϵ can be selected as phase-cells. In the most probable state of the system of structureless molecules the number of particles whose phases lie in such an energy-shell is

$$C v e^{-\mu \epsilon} \epsilon^{\frac{1}{2}} \delta \epsilon \quad . \quad . \quad . \quad . \quad (16.2.5)$$

where C is determined by

$$C v \int_0^{\infty} \epsilon^{\frac{1}{2}} e^{-\mu \epsilon} d\epsilon = n.$$

When we pass to the question of internal degrees of freedom, the matter can be treated in an analogous way. Leaving aside in its turn and for the moment the question of the general position and motion of a molecule, suppose the internal structure of the molecule to be defined by values of certain co-ordinates q_1, q_2, \dots, q_f and momenta p_1, p_2, \dots, p_f . These can at the moment, pending a fuller account of the dynamics of such systems, be thought of as a suitable number of Cartesian co-ordinates or polar co-ordinates of sub-particles with reference to origin and axes in the molecule, and the linear momenta or linear and angular momenta accompanying them. The salient point to bear in mind at present is that the product of any co-ordinate and its corresponding momentum has the physical dimensions of action (energy \times time). The internal energy of a particle will be given by some function of the q , and p , $\phi(q_1, \dots, q_f, p_1, \dots, p_f)$, or briefly $\phi(q, p)$. In the $2f$ -dimensional phase-diagram, the phases satisfying

$$\phi(q, p) = \epsilon \quad . \quad . \quad . \quad . \quad (16.2.6)$$

occupy a $2f - 1$ dimensional extension. The $2f$ -dimensional region which "lies between" (16.2.6) and

$$\phi(q, p) = \epsilon + \delta\epsilon \quad . \quad . \quad . \quad (16.2.7)$$

contains those phases which satisfy any equation such as

$$\phi(q, p) = c$$

where c has a value between ϵ and $\epsilon + \delta\epsilon$. It will have a magnitude

$$\chi(\epsilon) \delta\epsilon$$

where $\chi(\epsilon)$ is a function of ϵ , involving of course such constants as are present in the functional form of $\phi(q, p)$. In the most probable state of the system of molecules the number whose internal co-ordinates and momenta will at any moment lie in the energy-shell between (16.2.6) and (16.2.7) are given by an expression involving

$$e^{-\epsilon} \chi(\epsilon) \delta\epsilon.$$

16.3 Energy-Hypersurfaces and Paths.—Following the representative point of any particle, this will travel about the phase-diagram in a fortuitous sort of way. For a time it may remain on an energy-hypersurface; it is experiencing no influence from other particles or radiation. But at times its path will be stretched from some point on one hypersurface to a point on another; it is then under such influences. Let us consider a little more closely the paths when the particle is undisturbed and still, for convenience, confine ourselves to the internal motion. The co-ordinates q and momenta p can theoretically be determined from the equations of motion. They are then expressed, each as a function of the time t and certain constants.* Of these constants a certain number will depend on the internal structure of the molecule; we shall denote them by a_1, a_2, \dots . Others, $2f$, in number, are introduced in the integration of the equations of motion. These integration constants we shall denote by b_1, b_2, \dots, b_{2f} . We then have

* Chapter XXIV. will give a fuller explanation of these statements which may be accepted now without question.

$$\begin{aligned}
q_1 &= \theta_1(t, a, b) \\
&\dots \dots \dots (16.3.1) \\
q_f &= \theta_f(t, a, b) \\
p_1 &= \psi_1(t, a, b) \\
&\dots \dots \dots \\
p_f &= \psi_f(t, a, b)
\end{aligned}$$

where $\theta_1(\dots), \dots, \psi_f(\dots)$ are $2f$ functional forms. If we give a definite set of values to the b constants, then the sets of values acquired by q_1, \dots, p_f , as we vary t from $-\infty$ to $+\infty$, constitute a path of the particle in undisturbed motion. The b constants vary from path to path. But the a constants have the same values in all paths; they are characteristic of the molecule itself, and its particular structure. We represented the energy by $\phi(q, p)$. If in this function we substitute for the q_r and p_r the functions $\theta_r(\dots)$ and $\psi_r(\dots)$, the terms involving t must vanish identically, since the energy of the particle is constant in undisturbed motion, and $\phi(q, p)$ is transformed into a function of the a_r and b_r^i constants, say $\psi(a_1, a_2, \dots, b_1, b_2, \dots)$. All this is briefly and picturesquely expressed by saying that any path "lies on" some energy-hypersurface. If the energy is ϵ , then, of course,

$$\psi(a_1, a_2, \dots, b_1, b_2, \dots) = \epsilon \quad (16.3.2)$$

Now, in general, this equation can be satisfied by an infinity of different values for the set of constants b_1, b_2, \dots, b_{2f} ; for (16.3.2) is only one equation in $2f$ quantities b_1, b_2, \dots, b_{2f} . Thus on one energy-hypersurface there is in general an infinity of undisturbed paths of the particle. Of course it might happen that only one of the b_r constants appears in the function $\psi(a, b)$, and if it appears in a term of the first degree, there is only one path. Nevertheless, whether the paths are numerous or not, there is no guarantee that they "fill up" completely the extension (of dimensionality $2f - 1$) of the hypersurface. Giving every value from $-\infty$ to $+\infty$ to t , and all the suitable values to b_1, b_2, \dots, b_{2f} , we obtain an infinity of sets of values of $q_1, \dots, q_f, p_1, \dots, p_f$, satisfying

$$\phi(q, p) = \epsilon,$$

but that is no proof that we have thereby obtained all the sets of values which satisfy this equation. This point should not be overlooked. It has an important bearing on the arguments which will be advanced later to justify the postulates of statistical mechanics.

16.4 Quantisation of the Paths. Degeneracy.—Still confining ourselves to the internal motion of the molecule, we know that any path* is characterised by the values of the f action-integrals which are derived in the analysis of the motion into its latent periodic elements. These are, in fact, functions of the constants, and, of course, will vary from path to path. Also the energy can be expressed as a function of these f action-integrals.

Quantisation of the paths is effected by selecting those values of the action-integrals which are whole-number multiples of h . This obviously selects certain energy-hypersurfaces as relevant in quantum atomic physics, the others being irrelevant. The journey of the representative point from one of the quantum hypersurfaces to another in a quantum jump is an occurrence whose details are not disclosed by any part of the theory of stationary states. It is regarded as occupying a time so brief that only one characteristic of it comes into the discussion, the amount of energy emitted or absorbed. The contrast to classical theory where the journey from one hypersurface to another during a period of disturbance is supposed to agree with the laws of dynamics, is marked. In quantum considerations, it is the quantum hypersurfaces which are all important, and the quantum paths on them. Interesting questions will arise as to the number of quantum paths on one energy-hypersurface. If in $E(J_1, J_2, \dots, J_f)$ we substitute $r_1 h, r_2 h, \dots, r_f h$ for the several J_r , we obtain a function $\epsilon(r_1, r_2, \dots, r_f)$ of the quantum-numbers of the path, which is equal to the energy corresponding to the hypersurface on which it lies. Now if the r_s variables were

* The internal motion is naturally visualised as the motion of several submolecular particles (atoms, electrons) in orbits; but do not confuse "path" with any particular orbit. The path is a synthesis not only of the geometric features of these orbits, but also of the actual conditions of movement of the sub-particles in them.

capable of taking any values, then in general many quantum paths would lie on a hypersurface, but as they are integers, we cannot maintain this statement; for we cannot assert that in general an equation like

$$\epsilon(r_1, r_2, \dots, r_f) = c$$

can have a solution in integers at all for a given value of c , and if it has one such solution, we cannot therefore assert that it has any more such solutions than this one. Still, there are certain easily-defined cases in which there are more quantum paths than one on any of the quantum hypersurfaces. Thus, if the energy function $E(J)$ happens to be a function of $J_1 + J_2, J_3, J_4, \dots, J_f$, then $\epsilon(r)$ is a function of $r_1 + r_2, r_3, r_4, \dots, r_f$. Thus any pair of integral values of r_1 and r_2 which have the same sum will yield the same energy. But different values of r_1 and r_2 , even if they have the same sum, when combined with one set of values for r_3, r_4, \dots, r_f , correspond to different quantum paths which are therefore on the same energy-hypersurface. It will be recalled that the fundamental frequencies of the internal motions in the molecules are given by

$$\nu_r = \frac{\partial E(J)}{\partial J_r},$$

so the condition of affairs just mentioned means that $\nu_1 = \nu_2$, or two of the fundamental periods are the same. In reality, $E(J)$ is a function of only $f - 1$ variables, since the single variable, $J_1 + J_2$, takes the place of J_1 and J_2 . We cannot enter into the dynamical theory of this matter here, but the reader will probably not find much difficulty in accepting the statement that the motion appears to be one in which there are not f , but only $f - 1$, degrees of freedom. It is said to be "degenerate" on that account; the question is one of importance in statistical theory, as we shall see presently. As a matter of fact, any linear relation between the frequencies, such as

$$\alpha_1 \nu_1 + \alpha_2 \nu_2 + \dots + \alpha_f \nu_f = 0 \quad . \quad . \quad (16.4.1)$$

where the α_r are *positive or negative integers*, produces degeneracy.* The internal motion in the molecules appears to be deprived of one of its internal degrees of freedom ; but what is more germane to our purpose is that there are in such cases a number of different quantum paths on the same energy-hypersurface. If two relations, such as (16.4.1) hold, the system is doubly degenerate ; the molecule appears to have lost two of its internal degrees of freedom, and the possibility of multiplicity of paths on the same hypersurface is increased.

We saw that in statistical-mechanical theory the quantum paths take the place of equal-sized phase-cells in counting complexions. Thus in the most probable state of the system of molecules the number of molecules which are in the quantum-state denoted by the quantum-numbers r_1, r_2, \dots, r_f , is proportional to

$$\exp \left\{ - \frac{\epsilon(r_1, r_2, \dots, r_f)}{k\theta} \right\}.$$

If now there are w_s quantum paths on the energy-hypersurface corresponding to an energy ϵ_s of the molecule, then in the most probable state of the system the number of molecules having the energy ϵ_s is proportional to

$$w_s \exp \left\{ - \frac{\epsilon_s}{k\theta} \right\} . \quad . \quad . \quad . \quad (16.4.2)$$

If classical conditions held for the internal motion, it was pointed out that in the most probable state the number of molecules having a definite energy, ϵ would be really zero, *i.e.*, statistically. A statistical statement could only be made concerning molecules whose energies lie between ϵ and $\epsilon + \delta\epsilon$; the number is

$$- C e^{-\mu\epsilon} \chi(\epsilon) \delta\epsilon$$

The corresponding full statement for the quantum conditions is that the number of molecules which have an

* See the Appendix to the Chapter.

assigned energy ϵ consistent with one or more stationary states is

$$C w e^{-\mu\epsilon} h^f$$

where w is the number of states having this energy. The expression wh^f replaces $\chi(\epsilon) \delta\epsilon$. Both have of course the same physical dimensions, *viz.*, those of the f^{th} power of action.

APPENDIX TO CHAPTER XVI

It will be less troublesome to follow the discussion on degeneracy if we consider the condition (16.4.1) for three degrees of freedom. The reader can easily make the extension to any number. In that case there are three action-integrals, and the condition

$$a_1 \nu_1 + a_2 \nu_2 + a_3 \nu_3 = 0$$

where a_1, a_2, a_3 , are three integers, positive or negative, implies that

$$a_1 \frac{\partial E(J)}{\partial J_1} + a_2 \frac{\partial E(J)}{\partial J_2} + a_3 \frac{\partial E(J)}{\partial J_3} = 0.$$

Now introduce the substitution

$$\begin{aligned} I_1 &= a_{11} J_1 + a_{12} J_2 + a_{13} J_3 \\ I_2 &= a_{21} J_1 + a_{22} J_2 + a_{23} J_3 \\ I_3 &= a_{31} J_1 + a_{32} J_2 + a_{33} J_3 \end{aligned}$$

where the a_{rs} are integers. We can solve for the J_r in terms of the I_r and substitute in $E(J)$; the result is a function of I_1, I_2, I_3 , say $F(I)$. It is easy to see that

$$\begin{aligned} \frac{\partial E(J)}{\partial J_1} &= \frac{\partial F(I)}{\partial I_1} \cdot \frac{\partial I_1}{\partial J_1} + \frac{\partial F(I)}{\partial I_2} \cdot \frac{\partial I_2}{\partial J_1} + \frac{\partial F(I)}{\partial I_3} \cdot \frac{\partial I_3}{\partial J_1} \\ &= a_{11} \frac{\partial F(I)}{\partial I_1} + a_{21} \frac{\partial F(I)}{\partial I_2} + a_{31} \frac{\partial F(I)}{\partial I_3} \end{aligned}$$

and similarly

$$\begin{aligned} \frac{\partial E(J)}{\partial J_2} &= a_{12} \frac{\partial F(I)}{\partial I_1} + a_{22} \frac{\partial F(I)}{\partial I_2} + a_{32} \frac{\partial F(I)}{\partial I_3} \\ \frac{\partial E(J)}{\partial J_3} &= a_{13} \frac{\partial F(I)}{\partial I_1} + a_{23} \frac{\partial F(I)}{\partial I_2} + a_{33} \frac{\partial F(I)}{\partial I_3} \end{aligned}$$

So that the condition for degeneracy, is satisfied if

$$\begin{aligned}a_{11} a_1 + a_{12} a_2 + a_{13} a_3 &= 0 \\a_{21} a_1 + a_{22} a_2 + a_{23} a_3 &= 0 \\a_{31} a_1 + a_{32} a_2 + a_{33} a_3 &= 0.\end{aligned}$$

Now if we choose any two integers m and n , we can find another number p such that

$$ma_1 + na_2 + pa_3 = 0.$$

If p is not an integer, it is nevertheless a commensurable number since a_1, a_2, a_3 are integers; hence, by clearing of fractions we find three *integers* b_1, b_2, b_3 , such that

$$b_1 a_1 + b_2 a_2 + b_3 a_3 = 0,$$

and from the method of finding them it would appear that there exists an unlimited number of ways of doing so. Thus the three conditions for degeneracy written above are perfectly feasible, but they would appear to be only three of an unlimited number of such conditions. As a matter of fact there is really one too many. It is a well-known theorem in simultaneous equations that we cannot satisfy three equations

$$\begin{aligned}a_{11} x + a_{12} y + a_{13} z &= 0 \\a_{21} x + a_{22} y + a_{23} z &= 0 \\a_{31} x + a_{32} y + a_{33} z &= 0\end{aligned}$$

simultaneously for any arbitrary values of the nine coefficients. If they are to be true simultaneously, then it must also be true that

$$\begin{aligned}a_{31} &= \lambda a_{11} + \mu a_{21} \\a_{32} &= \lambda a_{12} + \mu a_{22} \\a_{33} &= \lambda a_{13} + \mu a_{23}\end{aligned}$$

where λ and μ are some two multipliers. Thus it appears that

$$I_3 = \lambda I_1 + \mu I_2,$$

and thus we have reduced $E(J_1, J_2, J_3)$ to a function of two variables, I_1 and I_2 , since I_3 is a linear function of these two. The mechanical system then behaves as if it had only two independent action-integrals, two independent periods, and only two degrees of freedom.

When it comes to quantisation, we see that the energy,

being expressible as a function of I_1 and I_2 , is expressible also as a function $\psi(\rho, \sigma)$ of two integers ρ and σ , which are given by

$$\begin{aligned}\rho &= a_{11} r_1 + a_{12} r_2 + a_{13} r_3 \\ \sigma &= a_{21} r_1 + a_{22} r_2 + a_{23} r_3\end{aligned}$$

where r_1, r_2, r_3 , are the quantum numbers of a path. Clearly this is compatible with the same energy for different sets of values for r_1, r_2, r_3 . Thus the quantum numbers $r_1 + a_1, r_2 + a_2, r_3 + a_3$, would give the same ρ and σ , or for that matter, $r_1 + ka_1, r_2 + ka_2, r_3 + ka_3$, would do so likewise where k is any integer. Still the choice is not unlimited; for we must bear in mind that the quantum numbers must be positive integers, while a_1, a_2, a_3 are not all positive. This condition will, of course, limit the choice of suitable values of k .

It may be of interest to point out the general sort of evidence which experiment can give as to existence of degeneracy in atomic systems. The most notable example is the Zeemann effect. A spectral line of an atom is split by a magnetic field into a number of lines with slightly different wavelengths. This means that the mechanism in the atom has several different elements of periodicity which have the same frequency. The magnetic field affects each element rather differently, and the alteration of frequency produced is not quite the same in each case, and so each element gives unambiguous evidence of its presence.

CHAPTER XVII

QUANTUM THEORY OF THE SPECIFIC HEATS OF GASES

17.1 Specific Heat and the Internal Oscillations of the Molecules.—From the considerations outlined in the previous three chapters, we find that the internal motions of the molecules contribute to the energy-content of the system

$$C \sum \epsilon_s w_s e^{-\mu \epsilon_s}$$

where the summation is over all the energy hypersurfaces, and the constant C is determined by the equation

$$C \sum w_s e^{-\mu \epsilon_s} = n.$$

Let us represent the lowest quantum energy state by the suffix zero, and put $C e^{-\mu \epsilon_0} = C_0$. By Bohr's second postulate, if a quantum jump takes place from the hypersurface ϵ_s to the lowest quantum state, the frequency of the radiation emitted is ν_s where

$$\epsilon_s - \epsilon_0 = h\nu_s.$$

Thus

$$C_0 (1 + \sum_{s=1} w_s e^{-\mu h\nu_s}) = n,$$

and the energy-content is

$$C_0 (\epsilon_0 + \sum_{s=1} \epsilon_s w_s e^{-\mu h\nu_s}).$$

Combining these, we see that the energy-content is

$$\frac{n \cdot \epsilon_0 + \sum \epsilon_s w_s e^{-\mu h\nu_s}}{1 + \sum w_s e^{-\mu h\nu_s}} \quad . \quad . \quad . \quad (17.1.1)$$

and if we differentiate this expression with respect to θ , we obtain the contribution made by the internal motions of the molecule to the specific heat of the system of molecules. If we do so, we obtain an expression whose numerator is

$$\frac{n h}{k\theta^2} \left\{ \begin{aligned} &\sum \nu_s \epsilon_s w_s e^{-\mu h\nu_s} (1 + \sum w_u e^{-\mu h\nu_u}) \\ &- \sum \nu_u w_u e^{-\mu h\nu_u} (\epsilon_0 + \sum \epsilon_s w_s e^{-\mu h\nu_s}) \end{aligned} \right\}$$

and whose denominator is

$$(1 + \Sigma w_s e^{-\mu h \nu_s})^2.$$

The latter is positive and greater than unity, so the contribution to the specific heat turns out to be less than $n\hbar/k\theta^2$ multiplied by the sum of a number of terms such as

$$(\nu_s \epsilon_s + \nu_u \epsilon_u - \nu_u \epsilon_s - \nu_s \epsilon_u) w_s w_u e^{-\mu h(\nu_s + \nu_u)}$$

This latter expression is equal to

$$\begin{aligned} & (\nu_s - \nu_u) (\epsilon_s - \epsilon_u) w_s w_u e^{-\mu h(\nu_s + \nu_u)} \\ &= \frac{(\epsilon_s - \epsilon_u)^2}{h} w_s w_u e^{-\mu h(\nu_s + \nu_u)} \end{aligned}$$

Thus the contribution is less than

$$n k \Sigma \Sigma \left(\frac{\epsilon_s - \epsilon_u}{k\theta} \right)^2 w_s w_u e^{-\mu h(\nu_s + \nu_u)}$$

Now the frequencies involved are according to spectroscopic evidence in the ultra-violet, luminous or high infra-red ranges of the spectrum; their order of magnitude is certainly not lower than 10^{14} . That being so, it will be easily seen that for ordinary temperatures the value of the index in any exponential factor is numerically greater than 15, and in the majority very much greater. But e^{-15} and other experimental factors still smaller, will practically render the multiplier of nk in the previous expression negligible. The smallness of the contribution is still more marked for low temperatures. Only for very high temperatures would the internal degrees of freedom begin to contribute an appreciable fraction of nk or R for each degree of freedom in the internal structure of the molecule. In this way the quantum theory surmounts one of the difficulties of the older theory, which required for each degree of freedom a contribution to the specific heat of $R/2$ as regards kinetic energy and an amount of the same order of magnitude as regards potential energy. In general terms, and putting aside the rather clumsy expressions involved in the analysis, the spectroscopic evidence shows that the great majority of the molecules will be in the lowest internal quantum state, by reason of the smallness of the factors, such as $e^{-\mu h \nu_s}$. Thus the

internal energy will not differ much from $n\epsilon_0$. At a somewhat higher temperature there will be a very small change in the distribution of the molecules among the higher quantum states; the exponential terms are not seriously affected; practically the internal energy will still be $n\epsilon_0$, and the quotient of the change by the rise of temperature is insignificant. Only at extremely high temperatures when $k\theta$ would be approaching in value to some of the $h\nu_s$, would the change in internal energy with rising temperature begin to show itself in the specific heat.

17.2 Molecular Rotation and the Specific Heat of a Diatomic Gas.—The order of magnitude of the frequencies involved in electron motions within the atoms or even in the relative vibrations of the atoms constituting a molecule is therefore so great that no contribution to the specific heat of a gas can be expected from this quarter except at extremely high temperatures. Yet we know that the ordinary translatory movements of the gas molecules can only contribute an amount $3R/2$ to the thermal capacity of a body of gas, and this is too small under ordinary circumstances except for monatomic gases. We saw in Chapter V. that in the case of diatomic gases the balance, approximately R , could be accounted for reasonably enough by assuming a further two degrees of freedom involved in a rotation of the molecule about an axis at right angles to the line joining the centres of the two atoms; rotation about this latter line itself is excluded from consideration for reasons stated in that chapter. Nevertheless experiments, especially on hydrogen, show that this contribution does not remain even approximately near R as the temperature decreases; the evidence is very much in favour of the view that as the temperature approaches absolute zero, the contribution of molecular rotation to the specific heat diminishes asymptotically to zero. This suggests at once that in some way the rotational motion is quantised and not subject to classical equipartition, while the frequencies involved are of such magnitude that the average energy must be close to $k\theta$ for ordinary temperatures, but much less as θ decreases below normal values. Now the average energy is

$$\frac{h \nu}{\exp (h \nu / k \theta) - 1}$$

or

$$k \theta \frac{x}{e^x - 1},$$

where $x = h\nu/k\theta$. Putting $\theta = 300$, $k = 1.37 \times 10^{-16}$ and $h = 6.55 \times 10^{-27}$, we see that to make $x = 1$, ν must be of the order 6×10^{12} . Consequently frequencies between 10^{12} and 10^{13} would, at ordinary temperatures, approximately involve the classical partition of energy since for such conditions $x/(e^x - 1)$ would approximate to unity. But at much lower temperatures x would increase to the order of magnitude of 10 or even 100, and then $x/(e^x - 1)$ is practically negligible. Now, as a matter of fact, it has been discovered that in the absorption spectrum of water-vapour there actually exist some lines whose frequency are in the region about 5×10^{12} . These lines are usually referred to as the rotation-spectrum; and as a piece of additional evidence there has also been observed a well-marked effect produced by rotations of such frequencies on the lines in the infra-red of order 10^{14} , which arise from the atomic vibrations in the molecules of water-vapour and the hydrogen halides.

To be sure we are not dealing here with an oscillator in the Planck sense, having one frequency for all amplitudes, and the treatment just outlined is too inadequate. But a method of quantising a rotation, easily deduced from the considerations of Chapter XV., forms the basis of a theory which accounts for the behaviour of diatomic gases as regards their specific heats, apart from some minor discrepancies, which appear to arise rather from our lack of knowledge of the actual structure of the molecules than from any serious deficiency in the theory.

A diatomic molecule pictured as a dumb-bell has the line joining the atoms as one principal axis of inertia. Any two lines at right angles to this and to each other and passing through the centre of gravity can be taken as two other principal axes of rotation. The atom is a "symmetrical top," but will the reader carefully bear in mind that rotation about the axis of symmetry, *i.e.*, the line joining the atoms,

does not come into consideration? One reason for excluding this rotation was given earlier in the classical treatment; another reason, more in keeping with quantum ideas, will emerge presently. It is with rotations about axes at right angles to the line of symmetry that we are concerned. Let A be the symbol for the moment of inertia of the atom about such an axis. This is as a matter of fact equal to $M_1 r_1^2 + M_2 r_2^2$ where M_1 and M_2 are the masses of the atoms, and r_1 and r_2 are their distances from the centre of gravity, and it is not difficult to show that this is also equal to Ma^2 where a is the distance separating the atom-centres and

$$\frac{1}{M} = \frac{1}{M_1} + \frac{1}{M_2}.$$

The angular momentum round the axis is $A\omega$ if ω is the angular velocity. The action accumulated in one period, *i.e.*, in one rotation is then $2\pi A\omega$, and so, according to quantum views, rotations with *any* angular velocity cannot exist for an interval of undisturbed rotation, but only rotations for which the action-integral $2\pi A\omega$ has a value such as h , $2h$, $3h$, etc.* Hence the "rotator" can only have one of a series of discrete angular velocities ω_1 , ω_2 , ω_3 , where

$$\omega_r = \frac{rh}{2\pi A} \quad . \quad . \quad . \quad . \quad (17.2.1)$$

When rotating with one of these velocities it is in a quantum state defined for the moment by one quantum number r . But one number is really insufficient. We have two degrees of freedom to deal with (the third, rotation around the axis of symmetry, has been definitely excluded), and we must have two quantum numbers. We have here, in fact, an example of degeneracy, and in the early days of the theory this feature of the situation caused some trouble for a reason which will appear presently. Leaving this ambiguity on one side for a moment, we see that the energies of the quantum

* The reader will observe that angular momentum being the product of mass, distance squared and angular velocity actually has the same physical dimensions as action.

states of the rotator defined by (17. 2. 1) are given by equations such as

$$\begin{aligned}\epsilon_r &= \frac{1}{2} A \omega_r^2 \\ &= r^2 \frac{h^2}{8 \pi^2 A} \quad . \quad . \quad . \quad (17.2.2)\end{aligned}$$

Thus the energy in a quantum state varies as the square of the quantum number, a rule quite distinct from the rule which holds for a Planck oscillator ; in that case the variation is with the first power. We would now be in a position to obtain the average energy of a molecular rotator in the system if we knew the number of quantum states consistent with this energy, for as we have seen, it is equal to

$$\frac{\sum_0^{\infty} w_r \epsilon_r e^{-\mu \epsilon_r}}{\sum_0^{\infty} w_r e^{-\mu \epsilon_r}} \quad . \quad . \quad . \quad (17.2.3)$$

One of the earliest attempts to use this expression was based on the assumption that the w_r are each unity and that the result thus obtained should be doubled so as to take account of the two degrees of freedom really involved in rotation about an axis at right angles to the symmetry-line of the molecule. It will be instructive to carry out this evaluation before proceeding to later attempts to cope with the difficulty. On such a view the rotational energy of the system is

$$\begin{aligned}& 2 n \frac{\sum_0^{\infty} \epsilon_r e^{-\mu \epsilon_r}}{\sum_0^{\infty} e^{-\mu \epsilon_r}} \\ &= -2 n \frac{d}{d\mu} \log \left\{ \sum_0^{\infty} e^{-\mu \epsilon_r} \right\} \\ &= -2 n \frac{d}{d\mu} \log \left\{ \sum_0^{\infty} e^{-a r^2} \right\}\end{aligned}$$

where

$$a = \frac{\mu h^2}{8 \pi^2 A}.$$

The rotational part of the thermal capacity of the n molecules of gas is then equal to

$$\begin{aligned} &= -2n \frac{d}{d\theta} \frac{d}{d\mu} \log \left\{ \sum_0^{\infty} e^{-a r^2} \right\} \\ &= 2nk\mu^2 \frac{d^2}{d\mu^2} \log \left\{ \sum_0^{\infty} e^{-a r^2} \right\} \end{aligned}$$

At low temperatures μ , and therefore a , are relatively large. The series $\sum e^{-a r^2}$ practically reduces to $1 + e^{-a}$, and the logarithm of this to e^{-a} ; thus the rotational thermal capacity is equal to

$$\begin{aligned} &2R\mu^2 \frac{d^2}{d\mu^2} e^{-a} \\ &= 2R\mu^2 \left(\frac{h^2}{8\pi^2 A} \right)^2 e^{-a}, \end{aligned}$$

and since for large values of μ or a , the factor e^{-a} "swamps" μ^2 , this has a limit zero as μ increases indefinitely. For high temperatures a is small and since

$$\begin{aligned} &1 + e^{-a} + e^{-4a} + e^{-9a} + \dots \\ &= a^{-\frac{1}{2}} \{ x_1 + e^{-x_1^2} (x_2 - x_1) + e^{-x_2^2} (x_3 - x_2) + e^{-x_3^2} \\ &\quad (x_4 - x_3) + \dots \} \end{aligned}$$

where $x_1 = a^{\frac{1}{2}}$, $x_2 = 2a^{\frac{1}{2}}$, $x_3 = 3a^{\frac{1}{2}}$, etc., the series $\sum e^{-a r^2}$ can be approximately written as a definite integral

$$a^{-\frac{1}{2}} \int_0^{\infty} e^{-x^2} dx,$$

which is $\frac{1}{2} (\pi/a)^{\frac{1}{2}}$. Thus at high temperatures the rotational thermal capacity has as its limit

$$2R\mu^2 \frac{d^2}{d\mu^2} \log \frac{1}{2} \left(\frac{\pi}{a} \right)^{\frac{1}{2}},$$

which is equal to

$$\begin{aligned} &-2R\mu^2 \frac{d^2}{d\mu^2} \log \mu^{\frac{1}{2}} \\ &= R. \end{aligned}$$

The conclusions concerning the extreme limits are quite satisfactory; but, unfortunately, a closer investigation shows

that the thermal capacity rises to a maximum above R and sinks to a minimum below it before reaching the limit R . The experimental observations do not bear out this conclusion. Various other suggestions were made for dealing with the doubtful situation arising from the degeneracy of the motion, but all suffer more or less from the defect mentioned above, *viz.*, a tendency for the computed value to rise somewhat above the experimental value. Still they are an improvement on the earliest result obtained by the mere doubling method. The way in which the degeneracy of the motion is removed involves a rather wider knowledge of dynamical science than is assumed in this book. It must suffice to say that one plausible suggestion leads to the conclusion that there are really r different quantum states with the energy $r^2 h^2 / 8 \pi^2 A$, and so w_r should be put equal to r . Incidentally, this implies that in no state is the energy of rotation absolutely zero, the lowest quantum state has the energy of rotation $h^2 / 8 \pi^2 A$. This feature, *viz.*, that the lowest quantum state is not one devoid of rotational energy, is a common feature of all the hypotheses used to explain not only the thermal behaviour but also the results of spectroscopic analysis. In the same manner as we proceeded above, we now find that the rotational thermal capacity of n molecules is

$$R \mu^2 \frac{d^2}{d\mu^2} \log \sum_{r=1}^{\infty} (r e^{-ar^2})$$

At low temperatures this vanishes in the limit and at high temperatures the series approaches the value of the definite integral

$$a^{-1} \int_0^{\infty} x e^{-x^2} dx,$$

i.e., $1/2a$, which gives us a value R for the above expression at the upper limit of θ . But computation of the series still shows a discrepancy at moderate values. Thus about 200°A the computed value for hydrogen is $\cdot 82 R$ as against the experimental $\cdot 72 R$, a rather serious difference in view of the claims made by the experimentalists as regards the precision of their measurements. By the

time, however, we reach the temperatures of our normal surroundings, the discrepancy disappears, the values at freezing point of water being $\cdot 936$ R and $\cdot 937$ R respectively. The reader may recall the statement made earlier that recent spectroscopic work calls for "half-quantum numbers" in certain cases, meaning that although the quantum numbers increase by integral amounts from quantum state to quantum state, they are not necessarily integers themselves, but may have values such as $\cdot 5$, $1\cdot 5$, $2\cdot 5$, etc. This suggestion has been tried in this problem, and r being treated this way, it is found that w_r can either have the series of values 2, 4, 6, 8, or 1, 3, 5, 7, In either case this method gives better agreement with experimental facts than those based on integral values of the quantum numbers. As mentioned above, the source of the discrepancies may lie in the assumption of a constant A throughout; at higher temperatures there may be a "stretching" of the molecules owing to increased rotation and some change in the moment of inertia. The computations incidentally enable us to find a numerical value for A ; the values differ somewhat according to the method used, but they all agree in giving something of the order of magnitude 10^{-41} in C.G.S. units. This result is of the same order of magnitude as the values obtained from the observation of the rotation spectra and rotation-vibration spectra of vapours of water and the hydrogen halides, and is consistent with the value 10^{-24} gram for the mass of the hydrogen atom and $\cdot 5 \times 10^{-8}$ cm. for the diameter of the hydrogen atom. The latter are derived from the kinetic theory of gases or from Bohr's theory of the Balmer series, and it is assumed that the atoms in the molecule are close together.

We can now give the very simple explanation on quantum lines why we leave out of consideration rotation round the axis of symmetry of the molecule. The moment of inertia of the molecule round this axis is much smaller than A . All our present knowledge of atomic structure points to the conclusion that the mass of an atom is practically concentrated in the small nucleus, whose linear dimensions are of a much smaller order of magnitude than the radius of the

atom itself, *i.e.*, the radius of the outer electron orbits in the normal state of the atom. This latter radius is the order of magnitude of the distances of the atom centres from the centre of gravity which are used in calculating A ; but in calculating the moment of inertia around the axis of symmetry we would use distances of an order of magnitude given by the size of the nucleus. Call this latter moment of inertia C . If rotation about this axis came into play, the smallest possible angular velocity would be given by $h/2\pi C$ and the corresponding energy by $h^2/8\pi^2 C$. In comparison with $h^2/8\pi^2 A$, this would be very large ; the chance, therefore of a molecule being in the lowest quantum state of rotation around the axis of symmetry would be very small relative to the chance of it being in the lowest, or even in many a higher quantum state of rotation around axes at right angles to the symmetrical line. Molecules rotating round the axis of symmetry are in consequence too few in number to affect the final result.

CHAPTER XVIII

THE ELASTIC SPECTRUM OF A LINEAR LATTICE OF COHERING PARTICLES

18.1 The “Co-ordination” of a Chain of Particles.—For a real understanding of the manner in which the quantum hypothesis can be applied in the treatment of the specific heats of solid bodies, it is necessary to know something of the mathematical method by means of which the analysis of the irregular heat motions of the atoms into component simple vibrations is effected. The reader is probably aware that the physical and chemical facts concerning crystalline materials support the view that a “molecule” is apt to lose its identity in a solid. The constituent atoms of the molecules are arranged in space lattices, corresponding atoms of each molecule forming one lattice, other corresponding atoms forming another lattice, the lattices interpenetrating one another. Under such an arrangement it is hardly possible to say that one particular atom is associated with another particular atom to form a molecule. The partnerships set up when the substance is liquefied or vaporised hardly exist in the solid state. We shall, therefore, take as an ideal simple solid a group of particles of one kind arranged in a cubical lattice. This will form a convenient model for a monatomic solid.

In presenting the mathematical method referred to, it will be advisable to show its application in the first instance to something even simpler than the ideal solid, *viz.*, a row of particles cohering together by reason of strong attractions to form a chain, which, however, is not really rigid, but is capable of oscillating and displaying an enormous number of forms following one another in a manner determined by dynamical laws.

Every one with a musical ear can detect in the sound of a

note played on any instrument a series of simple notes with definitely related pitches, the so-called fundamental tone and its overtones. It is well known that these sound sensations are related to vibrations in the sounding body which can be analysed into more elementary vibrations each having a definite frequency. One of the most customary ways of illustrating this fact in works on Acoustics is to take the violin or piano string as an example. To apply the mathematical method, in its most simple form, we idealise these and conceive a string without any physical property, except length, mass and the capacity to support a tension and a slight stretching without breaking. It is in the first instance regarded as a linear continuum, so that the smallest fraction of the distance between its ends contains its proportional amount of mass. When such a string vibrates, we can imagine that its form at any instant can be rendered permanent for a while, so that we can study it at leisure. A cinematograph film of its behaviour, for example, can be stopped with a particular picture showing. The possible shapes have an infinite variety and complexity, yet they can be dealt with in a very powerful and elegant manner by a famous theorem due to Fourier. The geometry looks absolutely unmanageable, but the analysis is not at all difficult to understand. Let us assume that the string is fastened at its two ends. Distance from one of these ends along the string direction we shall denote by the symbol x , the whole length being l . Let us also for convenience assume that the vibrations are confined to one plane, *i.e.*, that each element of the string has only one degree of freedom. The displacement of an element in this plane from its equilibrium position, and, of course, at right angles to the direction of the string, we shall denote by ζ . The fact that the string has a definite shape at all at our moment of observation is expressed by saying that ζ is a function of x . In fact, when we write

$$\zeta = \psi(x),$$

we mean this. We have written down the "equation of the curve." Yet if we should glance at any of the shapes of vibrating strings that have been actually obtained with

violins, etc., we might well be dubious about the possibility of finding the actual "form" of the function $\psi(x)$. Yet there is a way of doing it which enables us to obtain $\psi(x)$ approximately with the possibility of carrying the approximation to any degree of accuracy necessary. Formal proof cannot be given here, but reference to any standard text on the calculus will substantiate the following result

$$\psi(x) = q_1 \sin \frac{\pi x}{l} + q_2 \sin \frac{2\pi x}{l} + \dots + q_r \sin \frac{r\pi x}{l} + \dots \text{ad inf.} \quad (18.1.1)$$

where the coefficients are definite integrals defined thus:—

$$q_r = \frac{2}{l} \int_0^l \psi(x) \sin \frac{r\pi x}{l} dx.$$

If the shape were actually drawn on a sheet of paper, we could, by multiplying each ordinate by the value of $\sin r\pi x/l$ at the point, obtain a new curve whose area would be the coefficient q_r multiplied by $l/2$. Work of a kind analogous to this is actually carried out to-day for practical ends, *e.g.*, in analysis of the tides. The reader will therefore realise that the statement that we could find the equation of the curve to any desired accuracy is not merely "theoretical;" it is quite practicable, if somewhat tedious at times. The salvation of the practicability lies in the fact that in a great many cases the series is so highly convergent that a half-dozen terms or even fewer serve very well. (In the most highly developed "harmonic analysis" of the tides at the present day, investigators seldom use more than two dozen harmonic constituents.) Even such an apparently intractable shape as a "zig-zag" is extremely well represented by six or seven terms.

So far this is a matter of geometry and analysis. Now we take up the kinematic side of the matter. The string does not stay in this shape. Shape after shape follow in a continuous succession depending on the tightness of the string and the shape from which we "let go." In the analysis this succession of shapes corresponds to a succession of values for the group of coefficients, q_r . Each of these is in fact a function

of time. If we knew what these functions were, we would have in that knowledge summarised the whole history of the string's behaviour. In short, q_1, q_2, \dots are "co-ordinates of the string." Here we take a more general attitude towards the word, co-ordinate, than hitherto. It is not to be merely restricted to Cartesian or polar methods of specifying the configuration of a system. This will, in fact, be a useful illustration to fall back on when we come to treat the most general way of stating the laws of dynamics in a later chapter. Any set of quantities which when known specify precisely the complete configuration of a system can be regarded as co-ordinates of the system. The very name "arranged together," suggests this.

If now we wish to find the functional forms which show how the various q_r depend on t , we must naturally use the laws of dynamics. It is known from the application of these that the displacement ζ is a function of x and t which satisfies the partial differential equation

$$T \frac{\partial^2 \zeta}{\partial x^2} = M \frac{\partial^2 \zeta}{\partial t^2}$$

where T is the tension of the string, and M is the mass of unit length of it. From this and equation (18.1.1) it follows that

$$\frac{\pi^2 T}{l^2} \sum_{r=1}^{\infty} r^2 q_r \sin \frac{r \pi x}{l} = M \sum_{r=1}^{\infty} \frac{d^2 q_r}{dt^2} \sin \frac{r \pi x}{l}$$

If this is to be true for any value of x , it follows that each q_r satisfies an equation of the type

$$\frac{d^2 q_r}{dt^2} = r^2 \frac{\pi^2 T}{l^2 M} q_r.$$

Hence

$$q_r = a_r \sin (\omega_r t - \epsilon_r) \quad . \quad . \quad (18.1.2)$$

where

$$\omega_r = r \frac{\pi}{l} \left(\frac{T}{M} \right)^{\frac{1}{2}} \quad . \quad . \quad . \quad (18.1.3)$$

and a_r and ϵ_r are arbitrary constants. The constants ω_r are, of course, independent of the initial conditions; they are

determined entirely by the nature of the system. The ω_r thus form a harmonic series of pulsations (pulsation is $2\pi \times$ frequency) whose fundamental is $(\pi/l) \cdot (T/M)^{\frac{1}{2}}$. On the other hand, the a_r and the ϵ_r are the usual integration constants entering into the solution in the integration of the equations of motion. They are arbitrary in the sense that if we start the string to vibrate by releasing it from one configuration, and then give it another vibration with a different initial form, the two sets of a_r and ϵ_r will be different. A glance at (18.1.2) will justify the use of the word "amplitude" for the a_r , but again in a more general sense than hitherto, not being confined to the amount of excursion from side to side which any element of the string makes. To make this clear, let us suppose that we choose all the a_r to be zero except a_1 ; all the q_r are also zero except q_1 , and we find for the displacement at time t of an element of the string situated at x the result

$$a_1 \sin(\omega_1 t - \epsilon_1) \sin \frac{\pi x}{l}.$$

If $x = 0$ or l , this is zero, as it must be since the ends are fixed; if $x = l/2$, the vibration is $a_1 \sin(\omega_1 t - \epsilon_1)$, and so a_1 is the amplitude, in the ordinary sense, of the vibration of the middle element of the string; but for any other position this is not so; the amplitude, in the customary sense, is $a_1 \sin(\pi x/l)$, which gradually decreases to zero as we approach either end. The string is then vibrating as a whole between two extreme sine forms

$$\zeta = a_1 \sin \frac{\pi x}{l}$$

$$\text{and} \quad \zeta = -a_1 \sin \frac{\pi x}{l}.$$

This is its fundamental vibration. If, however, we make all the a_r zero except a_2 , the displacement is given by

$$\zeta = a_2 \sin(\omega_2 t - \epsilon_2) \sin \frac{2\pi x}{l}.$$

This vanishes always at the middle point as well as at the ends; there is a "node" there. Only at the points of

quadrisection will the amplitude of displacement be a_2 ; there are two "antinodes" situated at those points. The string vibrates as it were in two halves between the extreme form

$$\zeta = a_2 \sin \frac{2\pi x}{l}$$

and the extreme form

$$\zeta = -a_2 \sin \frac{2\pi x}{l},$$

which are two complete sine-curves. The extension of this is obvious. The a_r are the amplitudes of the q_r co-ordinates. In the most complicated vibration of the string there are latent all the simple vibrations with an ascending series of harmonically related frequencies.

So far we have been dealing with the ideal string familiar in works on Acoustics. We must now point out how the result is modified if we replace the string by a chain of equally-spaced particles. For one thing we cannot be involved in an infinite series. If there are f particles, each with one degree of freedom, we only require f co-ordinates, no matter how chosen, to specify any configuration. So that gives us a broad hint that instead of an infinite series we must have something like this for an instantaneous form of the chain

$$\zeta_k = \phi_1 \sin \frac{\pi x_k}{l} + \phi_2 \sin \frac{2\pi x_k}{l} + \dots + \phi_f \sin \frac{f\pi x_k}{l}$$

where x_k is the distance of the k^{th} particle from one end and ζ_k its displacement. There is a distance $l/(f+1)$ between each particle, assuming that the two end ones are anchored to two immovable particles which we can suppose to be labelled 0 and $f+1$ respectively. Thus the previous equation can be written

$$\zeta_k = \phi_1 \sin \frac{k\pi}{f+1} + \phi_2 \sin \frac{2k\pi}{f+1} + \dots + \phi_f \sin \frac{fk\pi}{f+1} \quad (18.1.4)$$

(Incidentally this makes ξ_0 and ξ_{f+1} zero as it should.)

Now investigation shows that this surmise is quite correct,

and dynamical analysis * leads to a functional dependence of the f co-ordinates, $\phi_1, \phi_2, \dots \phi_f$ on t given by

$$\phi_r = a_r \sin (\kappa_r t - \epsilon_r),$$

where the a_r and ϵ_r are $2f$ arbitrary constants of integration, while the κ_r are f pulsations given by equations of the type

$$\kappa_r = 2 \left(\frac{T}{l'm} \right) \sin \frac{r \pi}{2(f+1)} \quad . \quad . \quad (18.1.5)$$

In this, T is still the tension, *i.e.*, the attraction between two neighbouring particles, m is the mass of one particle, *i.e.*, M/lf , and l' is the distance between particles or $l/(f+1)$.

The analogy between the ϕ_r and the q_r or between the ω_r and κ_r is obvious, and the question arises how far we can make use of the mathematical methods, suitable for dealing with a continuous medium, for the treatment of a medium with a discrete structure not only in the case actually under consideration, but also when three-dimensional bodies are in question. In the first place

$$\begin{aligned} \frac{T}{l'm} &= \frac{(f+1) T}{lm} \\ &= \frac{f(f+1)}{l^2} \cdot \frac{T}{M}. \end{aligned}$$

Further, if r is small compared with f , and f is a very great number

$$\sin \frac{r \pi}{2(f+1)} \doteq \frac{r \pi}{2(f+1)}$$

and

$$\kappa_r = \frac{r \pi}{l} \left(\frac{T}{M} \right)^{\frac{1}{2}}.$$

Thus, provided r is a reasonably small fraction of f , say 0.1 at most, there is practical equality between κ_r and ω_r . But as we ascend into the higher ranges of the κ_r frequencies, we cannot take them to be the ascending integral multiples of the fundamental frequency. However, we can anticipate that an application of the quantum theory will, in view of the general feature, which has already been illustrated in

* See Routh's *Rigid Dynamics*, Vol. II., Chapter IX., or Rayleigh's *Theory of Sound*, Vol. I., Chapter VI.

other connections concerning the decreasing significance of increasing frequency, turn out to produce results not far from the truth if we overlook the departure of the higher κ_r from the simple rule and assume that we are concerned with f harmonic frequencies which are all integral multiples of the frequency ν given by

$$\nu = \frac{1}{2l} \left(\frac{T}{M} \right)^{\frac{1}{2}}$$

That being so, we can plausibly assume that the ϕ_r agree with the q_r . The assumption is fully justified by a closer analysis in the cases where the Fourier series is convergent, and it is only with such cases that we are physically concerned.

Thus we have analysed the motion of any of the particles in an undisturbed vibration of the chain into simple harmonic constituents. If as before x stands for the distance of a particle from one end

$$\zeta = \sum_{r=1}^f a_r \sin \frac{r \pi x}{l} \sin \left(\frac{r \pi c t}{l} - \epsilon_r \right)$$

where

$$c = \left(\frac{T}{M} \right)^{\frac{1}{2}}.$$

It will be observed that the form of the chain exactly repeats itself when t increases by $2l/c$. This is the period of vibration; it is also the time in which anything travelling with a speed c would cover a distance equal to twice the length of the string. Indeed it is easily inferred from the general theory of the string that c or $(T/M)^{\frac{1}{2}}$ is the speed with which a transverse pulse would travel along an unlimited string with this tension and mass per unit length.

18.2 The Energy of the Chain.—The velocity of the particle whose distance from one end is x , is given by

$$\begin{aligned} \dot{\zeta} &= \sum_{r=1}^f \dot{q}_r \sin \frac{r \pi x}{l} \\ &= \sum_{r=1}^f \omega_r a_r \sin \frac{r \pi x}{l} \sin (\omega_r t - \epsilon_r). \end{aligned}$$

The kinetic energy is equal to $\frac{1}{2} M \int \dot{\xi}^2 dx$, and since

$$\int_0^l \sin \frac{r \pi x}{l} \sin \frac{s \pi x}{l} dx = 0 \text{ if } r \neq s \\ = \frac{l}{2} \text{ if } r = s$$

it is easy to see that the kinetic energy is

$$\frac{M l}{4} \sum_{r=1}^f \dot{q}_r^2 \quad . \quad . \quad . \quad . \quad . \quad (18.2.1)$$

As regards the potential energy in any configuration, it is the work required to produce the necessary stretching against the tension T . If in this configuration an element dx of the straight string is stretched to a length ds of an element of the curve, the potential energy in that element is $T (ds - dx)$ or $T (ds/dx - 1) dx$. But

$$\frac{ds}{dx} = \left\{ 1 + \left(\frac{d\zeta}{dx} \right)^2 \right\}^{\frac{1}{2}} \\ = \left\{ 1 + \frac{1}{2} \left(\frac{d\zeta}{dx} \right)^2 - \frac{1}{8} \left(\frac{d\zeta}{dx} \right)^4 + \dots \right\}$$

Neglecting terms beyond the second power, since $d\zeta/dx$ is small compared to unity, the potential energy of the string turns out to be

$$\frac{1}{2} T \int_0^l \left(\frac{d\zeta}{dx} \right)^2 dx,$$

and since

$$\frac{d\zeta}{dx} = \frac{\pi}{l} \sum_{r=1}^f r q_r \cos \frac{r \pi x}{l},$$

we can demonstrate as above that this energy is

$$\frac{\pi^2 T}{4 l} \sum_{r=1}^f r^2 q_r^2 \quad . \quad . \quad . \quad . \quad . \quad (18.2.2)$$

The kinetic energy and potential energy are by this analysis each separated into f parts, any one part being associated with a co-ordinate or its "velocity," where the word "velocity" is now used to indicate the rate of change of a generalised co-ordinate with respect to time and is not

necessarily the actual rate of movement of any particle. The similarity of the mathematical results to those for a system of simple oscillators is obvious, and one important feature is common to both, *viz.*, the equality of the average kinetic and potential energy of the linear lattice not only *in toto*, but also in its analysed parts. The average kinetic energy associated with the co-ordinate q_r is by (18.2.1)

$$\frac{M l}{8} a_r^2 \omega_r^2.$$

The average potential energy associated with q_r is by (18.2.2)

$$\frac{\pi^2 T}{8l} r^2 a_r^2,$$

and since $\omega_r^2 = r^2 (\pi/l)^2 (T/M)$, the equality follows. Thus *from the point of view of mathematical procedure*, the atomic chain can be regarded as a complex molecule with f internal degrees of freedom, represented by co-ordinates q_r and velocities \dot{q}_r , each following the simple harmonic law ; but it is necessary to be on guard against thinking that these are each related respectively to one link in the chain. All the q_r and the \dot{q}_r enter into the displacement and velocity of any individual atom of the chain.

18.3 The Statistics of a System of Atomic Chains.—Having thus dealt with the mechanical side of this problem as a preliminary illustration for the solid lattice, let us turn to the statistical aspect in a similar anticipatory vein.

Conceive that in a cubical enclosure an enormous number n of such chains each containing f atoms are stretched across from wall to wall, each anchored to the walls at its ends. The enclosure also contains gas molecules, so that the whole may be regarded as a mixture of gas molecules and “chain-molecules.” Exchange of energy goes on between the various members of the system, and we can work out in the usual manner the conditions of statistical equilibrium. Just as we have generalised the meaning of co-ordinate and velocity, so we can give a wider significance to momentum ; the full import of the step will be more apparent in Chapter XXIV, but we define the r^{th} “generalised component of

momentum " to be equal to the partial differential coefficient of the kinetic energy with respect to \dot{q}_r and denote it by p_r , so that in the present case

$$p_r = \frac{M l}{2} \dot{q}_r.$$

We can now represent the $2f$ quantities q_r, p_r in a $2f$ -dimensional phase-diagram or in f two-dimensional phase-diagrams, partitioning into phase-cells and counting the complexions in any statistical state just as before. If the reader feels any qualms about this procedure, feeling in a vague way that it is hardly as justifiable a process as when we represented actual co-ordinates and velocities or momenta of particles in the usual sense in a phase-diagram, he can banish them without any fear. He will see later that in so far as we can accept the procedure to be a justifiable one in the latter case, it is equally justifiable in the former. The particular character of the laws of dynamics, when given their most general mathematical form, takes care of that. Since the energy involves only squares of co-ordinates and momenta, we will arrive at the conclusion of equipartition of energy on the average among the various co-ordinates and momenta of the system, an amount $\frac{1}{2} k\theta$ to each, so that the whole system of n chains will, in an enclosure at temperature θ , contain energy of amount $nfk\theta$, *i.e.*, $fk\theta$ to each chain on the average.

If, however, we adopt quantum views, we select the quantum states of motion of a chain by giving various integral values to the f quantum numbers, s_1, s_2, \dots, s_f , defined by

$$\begin{aligned} \int p_1 dq_1 &= s_1 h \\ \int p_2 dq_2 &= s_2 h, \\ &\text{etc.,} \end{aligned}$$

where each integral is taken through a complete period of the corresponding co-ordinate, *i.e.*, $2\pi/\omega_r$ for q_r . These conditions give in each quantum state of the chain definite values to the amplitudes a_1, a_2, \dots, a_f , so that for example

the extreme forms between which a chain can swing to and fro have not an "infinite variety"; they form a discrete series of shapes. The energy in the state s_1, s_2, \dots, s_f , is equal to

$$s_1 h\nu_1 + s_2 h\nu_2 + \dots + s_f h\nu_f,$$

where $\nu_r = \omega_r/2\pi$, and in the most probable statistical state of the system of n chains the number which are in this quantum state is given by

$$C \exp \{ -\mu h (s_1 \nu_1 + s_2 \nu_2 + \dots + s_f \nu_f) \} \quad (18.3.1)$$

where the sum of all such expressions for all sets of values of the integers (s_1, s_2, \dots, s_f) is n . To find the average energy associated with a particular co-ordinate, say q_r , we have to work out the sum

$$C h\nu_r \Sigma s_r \exp \{ -\mu h (s_1 \nu_1 + s_2 \nu_2 + \dots + s_f \nu_f) \} \quad (18.3.2)$$

and divide by the sum of the expressions (18.3.1). It is easy to see that (18.3.2) is equal to

$$C (\Sigma s_r h\nu_r e^{-\mu s_r h\nu_r}) [\Sigma' \exp \{ -\mu h (s_1 \nu_1 + \dots + s_{r-1} \nu_{r-1} + s_{r+1} \nu_{r+1} + \dots + s_f \nu_f) \}],$$

where the Σ refers to summation of s_r from 0 to ∞ and the Σ' refers to summation with regard to the $f-1$ numbers $s_1, \dots, s_{r-1}, s_{r+1}, \dots, s_f$ over all possible values. The summation of (18.3.1) can also be represented by

$$C (\Sigma e^{-\mu s_r h\nu_r}) [\Sigma' \exp \{ -\mu h (s_1 \nu_1 + \dots + s_{r-1} \nu_{r-1} + s_{r+1} \nu_{r+1} + \dots + s_f \nu_f) \}].$$

Hence the average energy sought for is

$$\frac{\sum_{s_r=1}^{\infty} s_r h\nu_r e^{-\mu s_r h\nu_r}}{\sum_{s_r=1}^{\infty} e^{-\mu s_r h\nu_r}}$$

and this, as before, turns out to be

$$\frac{h\nu_r}{e^{\mu h\nu_r} - 1}.$$

On quantum views then the average energy of any chain in the system of chains is

$$\sum_{r=1}^f \frac{h\nu_r}{e^{\mu h\nu_r} - 1} \quad . \quad . \quad . \quad . \quad (18.3.3).$$

Since

$$\nu_r = r \frac{c}{2l},$$

we can write (18.3.3) as a definite integral regarding $c/2l$ as equivalent to a differential of frequency, $\delta\nu$. Thus the energy of the chain is

$$\frac{2l}{c} \int_0^{c/2l} \frac{h\nu}{e^{\mu h\nu} - 1} d\nu,$$

where the upper limit is $fc/2l$.

18.4 A Superficial Lattice.—A lattice of f particles arranged in a square of side l with i particles in a row, and i rows in the whole lattice ($i^2 = f$), can be treated in a very similar way, by identifying it for practical quantum purposes with its limit, *viz.*, a square elastic sheet with a mass M per unit area and a surface tension of T per unit length. The axes OX and OY lie along two sides of the sheet, and the sheet is supposed to be fixed along its boundary. It is known that if ζ is the displacement of a point (x, y) of the sheet, it is a function of x, y and t which satisfies the differential equation

$$\frac{\partial^2 \zeta}{\partial t^2} = c^2 \left(\frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} \right) \quad . \quad . \quad (18.4.1)$$

where

$$c^2 = \frac{T}{M}.$$

From this we find a solution which satisfies the boundary condition, that $\zeta = 0$ if $x = 0$ or l or if $y = 0$ or l . It is

$$\zeta = \sum_{r=1}^i \sum_{s=1}^i q_{rs} \sin \frac{r\pi x}{l} \sin \frac{s\pi y}{l},$$

where the q_{rs} are i^2 (or f) “co-ordinates” following a harmonic law of variation with time

$$q_{rs} = a_{rs} \sin (\omega_{rs} t - \epsilon_{rs}).$$

The a_{rs} (amplitudes) and ϵ_{rs} (epoch-angles) are arbitrary, but the natural pulsations of the lattice are given by

$$\omega_{rs} = \frac{\pi c}{l} (r^2 + s^2)^{\frac{1}{2}},$$

as can be easily verified from (18.4.1).

All the necessary details for quantisation can be easily supplied by the reader from the previous section, leading to the average energy of any atomic sheet (regarded as a complex molecule) belonging to a system of such sheets immersed in an atmosphere of gas molecules. It is

$$\sum_{r=1}^i \sum_{s=1}^i \frac{h\nu_{rs}}{e^{\mu h\nu_{rs}} - 1} \quad . \quad . \quad . \quad . \quad . \quad (18.4.2)$$

where
$$\nu_{rs} = \frac{c}{2l} (r^2 + s^2)^{\frac{1}{2}}.$$

To convert this into a definite integral in the same fashion as before, we observe that all the natural frequencies of a lattice which are not greater than a definite frequency ν , are the same as the number of pairs of *positive* integers the sum of whose squares is not greater than $(2l\nu/c)^2$. If the integers are plotted on squared paper ruled in unit lengths, we can realise that this number is the number of units of area in a quadrant of a circle drawn on this paper having a radius $2l\nu/c$; so it is

$$\frac{\pi l^2 \nu^2}{c^2}.$$

It follows that the number of natural frequencies of a lattice which lie in an elementary range ν to $\nu + \delta\nu$ is equal to

$$\frac{2\pi l^2 \nu}{c^2} \delta\nu \quad . \quad . \quad . \quad . \quad (18.4.3)$$

Thus to arrive at a definite integral which replaces (18.4.2) we must collect all the terms which correspond to $\nu + \delta\nu > \nu_{rs} > \nu$; these will supply one element to the integral; their individual value is taken as $h\nu/(e^{\mu h\nu} - 1)$, and the

number of them is (18.4.3). So the energy of a lattice on the average is

$$\frac{2\pi l^2}{c^2} \int_0^{\nu_f} \frac{h\nu^2}{e^{h\nu} - 1} d\nu \quad . \quad . \quad . \quad . \quad . \quad (18.4.4)$$

where

$$\begin{aligned} \nu_f &= \frac{c}{2l} (i^2 + i^2)^{\frac{1}{2}} \\ &= \frac{cf}{2l}. \end{aligned}$$

CHAPTER XIX

THE ELASTIC SPECTRUM OF A CUBICAL LATTICE

19.1 Some Preliminary Mathematical Statements.—

I. The wave equation.

If $f(x, y, z, t)$ is a function of four variables which satisfies the partial differential equation

$$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2 f}{\partial t^2},$$

it is called a “wave function.” It can be easily verified that any function of the expression $\alpha x + \beta y + \gamma z + \eta t$ is a wave function if the constants $\alpha, \beta, \gamma, \eta$, satisfy the relation

$$\alpha^2 + \beta^2 + \gamma^2 = \frac{\eta^2}{c^2} \quad . \quad . \quad . \quad (19.1.1)$$

The reason for the name is fairly obvious in this special case. If x, y, z, t , represent space and time co-ordinates, the value of the function at a place x_1, y_1, z_1 and time t_1 is the same as its value at the place x_2, y_2, z_2 and time t_2 provided

$$\alpha x_1 + \beta y_1 + \gamma z_1 + \eta t_1 = \alpha x_2 + \beta y_2 + \gamma z_2 + \eta t_2.$$

In short, the value which the function has on any plane

$$\alpha x + \beta y + \gamma z + \eta t_1 = 0$$

at time t_1 was or will be the value on the plane

$$\alpha x + \beta y + \gamma z + \eta t_2 = 0$$

at time t_2 . These planes are parallel to one another, and separated by a normal distance

$$\frac{\eta (t_1 \sim t_2)}{(\alpha^2 + \beta^2 + \gamma^2)^{\frac{1}{2}}},$$

i.e., according to (19.1.1) by the distance

$$c (t_1 \sim t_2).$$

This clearly can be taken to refer to the propagation of any value of the function in a direction defined by the direction cosines $\alpha/(\alpha^2 + \beta^2 + \gamma^2)^{\frac{1}{2}}$, etc., with a velocity c . The constancy of the value of the function over a whole plane at one instant is indicated by the use of the term "plane waves." As the wave-equation involves only first powers of the differential coefficients, the sum of any number of particular solutions is also a solution; so the propagation of any quantity by a group of plane waves in any number and in any directions would still yield at each point and instant, a quantity satisfying the wave equation.

An important special case of this occurs when the function $f(u)$ is a circular function $\sin u$ or $\cos u$. Expansion of these will also yield expressions such as

$$\frac{\sin \alpha x}{\cos \alpha x} \frac{\sin \beta y}{\cos \beta y} \frac{\sin \gamma z}{\cos \gamma z} \frac{\sin \eta t}{\cos \eta t}$$

(there being sixteen of them if we ring all the changes on the \sin and \cos). These individual expressions also satisfy the wave equation, as can be easily seen by noting that second differentiation with respect to x yields the same expression multiplied by minus α^2 , and so on.

II. Some remarks on the propagation of a disturbance through an elastic solid regarded as an ideal continuous medium will be necessary. The proof of the statements will be found in Love's *Treatise on the Theory of Elasticity*, or similar works.

An isotropic solid has two elastic moduli; the "bulk modulus" or the quotient of a uniform hydrostatic pressure by the fractional diminution in volume resulting from it; the "modulus of rigidity," or the quotient of a tangential stress applied to one face of a rectangular block by the shear of this plane past the opposite plane (supposed fixed), resulting from the stress. All the elastic constants of the material can be expressed in terms of these two moduli, denoted by κ and μ respectively.

If such a medium is distorted, and we represent by ξ, η, ζ , the components of the displacement of an element of the medium which was originally at a point x, y, z , then ξ, η, ζ

are each functions of the three variables x, y, z ,* the form of the three functions depending on the nature of the distortion. The quantity

$$\frac{\partial \xi}{\partial x} + \frac{\partial \eta}{\partial y} + \frac{\partial \zeta}{\partial z}$$

measures the "dilatation" or fractional change in volume of the element which is now at the point (x, y, z) . We shall denote this by θ . This element has not only suffered (in addition to its general displacement) a change in size, but also a rotation, ϖ , whose amount is defined by the three axial components

$$\tilde{\omega}_1 = \frac{1}{2} \left(\frac{\partial \zeta}{\partial y} - \frac{\partial \eta}{\partial z} \right), \tilde{\omega}_2 = \frac{1}{2} \left(\frac{\partial \xi}{\partial z} - \frac{\partial \zeta}{\partial x} \right), \tilde{\omega}_3 = \frac{1}{2} \left(\frac{\partial \eta}{\partial x} - \frac{\partial \xi}{\partial y} \right).$$

If instead of considering a static distortion, we consider a state of vibration existing in the body, then ξ, η, ζ , and of course $\varpi_1, \varpi_2, \varpi_3, \theta$, are functions of t as well as of x, y, z . It is known that θ satisfies the equation

$$\left(\kappa + \frac{4\mu}{3} \right) \left(\frac{\partial^2 \theta}{\partial x^2} + \frac{\partial^2 \theta}{\partial y^2} + \frac{\partial^2 \theta}{\partial z^2} \right) = \rho \frac{\partial^2 \theta}{\partial t^2} \quad . \quad . \quad (19.1.2)$$

so that the dilatation is propagated with a velocity equal to $\{(\kappa + 4\mu/3)/\rho\}^{\frac{1}{2}}$ where ρ is the density of the medium. Moreover, each component of the rotation satisfies an equation

$$\mu \left(\frac{\partial^2 \varpi_r}{\partial x^2} + \frac{\partial^2 \varpi_r}{\partial y^2} + \frac{\partial^2 \varpi_r}{\partial z^2} \right) = \rho \frac{\partial^2 \varpi_r}{\partial t^2} \quad . \quad . \quad (19.1.3)$$

This involves a wave propagation with a velocity $(\mu/\rho)^{\frac{1}{2}}$.

It should be realised that the components of the displacement (ξ, η, ζ) do not in general satisfy individually either of these wave equations. They could not, of course, satisfy both; i.e., definite values of ξ, η, ζ , could not be propagated with two velocities. However, there are special cases of vibratory motion in which no rotational motion exists, and then the displacement-components satisfy an equation similar to (19.1.2). There is one wave-velocity $\{(\kappa + 4\mu/3)/\rho\}^{\frac{1}{2}}$. It is known that for a single plane wave

* N.B.— ξ is in general not a function of x alone, but of all three variables (x, y, z) , etc.

propagated under such circumstances the displacement of an element is to and fro in a direction parallel to the direction of propagation of the wave. In other words a pure "dilatational" wave is longitudinal. There are also special cases in which no dilatation exists, the wave is purely a rotational one and the displacement-components then satisfy an equation similar to (19.1.3). Under these circumstances the displacement for a single plane wave takes the form of a vibration in the plane of the wave. Thus the rotational wave travels with a speed $(\mu/\rho)^{\frac{1}{2}}$ and is transverse.

The energy of strain in any element of volume is, per unit volume, known to be

$$\left(\kappa + \frac{4\mu}{3}\right) \theta^2 + 4\mu \left(\varpi_1^2 + \varpi_2^2 + \varpi_3^2\right) + 4\Sigma \left\{ \frac{\partial \xi}{\partial y} \frac{\partial \eta}{\partial z} - \frac{\partial \eta}{\partial y} \frac{\partial \xi}{\partial z} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19.1.4)$$

19.2 The Motion of a Cubical Lattice.—In the case of a linear or superficial lattice we were able to appeal to the results for a linear or superficial continuum, knowing that the discrepancy between the higher frequencies of the lattice and the corresponding frequencies of the continuum would be rendered negligible in quantum applications by the rapidly diminishing importance of the corresponding average energies. We make the same kind of appeal in the case of a cubical lattice and for the same reason; that is the justification for the rather long digression just finished. Without the information contained in it, any treatment of the lattice is apt to be very vague and not too cogent.

The lattice will have the atoms when at rest arranged in cubical order so that there are i atoms in any row of length l parallel to an edge. Thus in a volume l^3 there are f atoms where $f = i^3$. Any atom will be identified by three positive integers r, s, u ; r being its number in a row parallel to OX, s in a row parallel to OY, u in a row parallel to OZ. The suffix (rsu) will refer to this particle, and we can by methods similar to those used for a linear lattice express each component of the displacement of the atom (rsu) thus

$$\xi_{rsu} = \sum_{r=1}^i \sum_{s=1}^i \sum_{u=1}^i Q_{rsu} \sin \frac{r \pi x}{l} \sin \frac{s \pi y}{l} \sin \frac{u \pi z}{l} +$$

and similar expressions for η_{rsu} , ζ_{rsu} where the $+$ written at the end is to indicate that we can have seven more series if we like which involve terms such as $\cos r\phi \sin s\psi \sin u\chi$, $\cos r\phi \cos s\psi \sin u\chi$, $\cos r\phi \cos s\psi \cos u\chi$, etc., obtained by ringing the changes between \sin and \cos . (ϕ, ψ, χ are written for $\pi x/l$, etc., for convenience.) The Q_{rsu} are generalised co-ordinates, and a little thought will show that if we used all the eight series suggested there would be eight of them for a particular set of values of r, s, u . As there are three components of displacement, this would give us twenty-four co-ordinates for each set of (r, s, u) values. In consequence, when counting over all the terms of each series we should have $24 i^3$ or $24 f$ co-ordinates in all. But this is just eight times as many as are required to co-ordinate f particles each with three degrees of freedom. We clearly must limit the terms in the series in some way. In dealing with the linear and superficial lattices, we only retained sine terms, since only with them could we satisfy the conditions at the boundaries. The matter is not so simple here, but the clue to a successful reduction of terms lies in suitable boundary conditions, and in the fact that the expressions for ξ, η, ζ , must be separable into terms expressing the dilatational motion and terms expressing the rotational. We shall write down the following and justify them presently.

$$\begin{aligned} \xi_{rsu} &= \sum_{r=1}^i \sum_{s=1}^i \sum_{u=1}^i \left\{ \begin{aligned} q_1 \cos r\phi \sin s\psi \sin u\chi \\ + q'_1 \sin r\phi \cos s\psi \cos u\chi \end{aligned} \right\} \\ \eta_{rsu} &= \sum_{r=1}^i \sum_{s=1}^i \sum_{u=1}^i \left\{ \begin{aligned} q_2 \sin r\phi \cos s\psi \sin u\chi \\ + q'_2 \cos r\phi \sin s\psi \cos u\chi \end{aligned} \right\} \\ \zeta_{rsu} &= \sum_{r=1}^i \sum_{s=1}^i \sum_{u=1}^i \left\{ \begin{aligned} q_3 \sin r\phi \sin s\psi \cos u\chi \\ + q'_3 \cos r\phi \cos s\psi \sin u\chi \end{aligned} \right\} \end{aligned} \quad (19.2.1)$$

where the six quantities q_1, \dots, q'_3 have in general a different set of values for each choice of the integers r, s, u . In fact they should really be written as $(q_1)_{rsu}$, etc., but to avoid clumsiness, this complete suffixing is not used, since no ambiguity will arise on that account. There are $6f$

co-ordinates still involved, but assuming that q_1, q_2, q_3 refer solely to the dilatational motion and q'_1, q'_2, q'_3 to the rotational, we arrive at three conditions which must then hold for each set of six, and this reduces them effectively to three *independent* co-ordinates. To see this, let us work out the expressions for the dilatation and the components of rotation.

$$\theta = \frac{\pi}{l} \Sigma \Sigma \Sigma \left\{ \begin{aligned} &-(rq_1 + sq_2 + uq_3) \sin r\phi \sin s\psi \sin u\chi \\ &+ (rq'_1 + sq'_2 + uq'_3) \cos r\phi \cos s\psi \cos u\chi \end{aligned} \right\}$$

$$2\omega_1 = \frac{\pi}{l} \Sigma \Sigma \Sigma \left\{ \begin{aligned} &(sq_3 - uq_2) \sin r\phi \cos s\psi \cos u\chi - \\ &(sq'_3 - uq'_2) \cos r\phi \sin s\psi \sin u\chi \end{aligned} \right\}$$

and two similar results.

If the 3f co-ordinates q'_1, q'_2, q'_3 are only to supply the rotational part of the motion, then we must have a relation

$$rq'_1 + sq'_2 + uq'_3 = 0 \quad . \quad . \quad (19.2.2)$$

for each set of values of r, s, u . If q_1, q_2, q_3 are only to supply the dilatational part, then we must have the two relations

$$\frac{q_1}{r} = \frac{q_2}{s} = \frac{q_3}{u} \quad . \quad . \quad . \quad (19.2.3)$$

for each set of values of r, s, u . It will be seen that with these relations, the dilatation vanishes at the boundaries where $\sin \phi$ or $\sin \psi$ or $\sin \chi$ is zero; also the rotation at any point of one of the boundary faces is around a line normal to the face. To sum up, we can, putting $q_1 = rq, q_2 = sq, q_3 = uq$, write instead of (19.2.1)

$$\xi_{rsu} = \Sigma \Sigma \Sigma \left\{ \begin{aligned} &rq \cos r\phi \sin s\psi \sin u\chi \\ &+ q'_1 \sin r\phi \cos s\psi \cos u\chi \end{aligned} \right\} \quad . \quad (19.2.4)$$

and two similar equations, where the relation

$$rq'_1 + sq'_2 + uq'_3 = 0$$

holds, so that we have reduced the co-ordinates to three independent co-ordinates, q and any two of q'_1, q'_2, q'_3 , for each set of values for r, s, u .

The dilatation is then given by

$$\theta = -\frac{\pi}{l} \Sigma \Sigma \Sigma \{ (r^2 + s^2 + u^2) q \sin r\phi \sin s\psi \sin u\chi \} \quad (19.2.5)$$

and the rotation-components by

$$2\varpi_1 = -\frac{\pi}{\rho} \Sigma \Sigma \Sigma \{ (sq'_3 - uq'_2) \cos r\phi \sin s\psi \sin u\chi \} \quad (19.2.6)$$

and two similar expressions.

This is a matter of geometry and analysis. In a static distortion, the q and q' quantities are constants; but when vibration takes place they are functions of t , and we appeal to dynamics to discover the forms of the functions. A glance at (19.1.2) and (19.2.5) shows that

$$q = a_{rsu} \cos (\omega_{rsu} t - \epsilon_{rsu})$$

where

$$\left(\kappa + \frac{4}{3} \mu \right) \frac{\pi^2}{l^2} (r^2 + s^2 + u^2) = \rho \omega_{rsu}^2$$

or
$$\omega_{rsu} = \frac{\pi c}{l} (r^2 + s^2 + u^2)^{\frac{1}{2}} \quad . \quad . \quad (19.2.7)$$

c being the velocity of a longitudinal wave through the body.

Similarly the first of (19.1.3) and the first of (19.2.6) show that

$$sq'_3 - uq'_2 \propto \cos (\omega'_{rsu} t - \epsilon'_{rsu})$$

where

$$\omega'_{rsu} = \frac{\pi c'}{l} (r^2 + s^2 + u^2)^{\frac{1}{2}} \quad . \quad . \quad (19.2.8)$$

c' being the velocity of a transverse wave. Two similar proportionalities for $uq'_1 - rq'_3$ and $rq'_2 - sq'_1$ show that

$$\begin{aligned} q'_1 &= a'_{rsu} \cos (\omega'_{rsu} t - \epsilon'_{rsu}) \\ q'_2 &= b'_{rsu} \cos (\omega'_{rsu} t - \epsilon'_{rsu}) \\ q'_3 &= c'_{rsu} \cos (\omega'_{rsu} t - \epsilon'_{rsu}) \end{aligned}$$

where

$$r a'_{rsu} + s b'_{rsu} + u c'_{rsu} = 0.$$

19.3 The Energy of the Lattice.—The reader will probably be anticipating the direction in which the argument is going, but to complete it we must form the expression for the energy and show that it involves only *squares* of the q , q' and the \dot{q} , \dot{q}' . This may appear to be an appalling task in view of the complexity of the expressions obtained. Fortunately

it is easy to show that an enormous cancellation of terms takes place automatically.

Let us deal with the kinetic energy first. This is obtained by putting dots over the q and q' in (19.2.4), then squaring, multiplying by $\frac{1}{2} \rho \, dx \, dy \, dz$, and integrating between the limits 0 and l for x, y, z . Now in such integrations all integrands which involve sines or cosines of *different* multiples of ϕ (i.e., $\pi x/l$), or of ψ , or of χ , add nothing to the result, since

$$\int_0^l \sin \frac{r \pi x}{l} \sin \frac{r' \pi x}{l} dx = 0 \text{ if } r \neq r'$$

$$= \frac{l}{2} \text{ if } r = r'$$

$$\int_0^l \cos \frac{r \pi x}{l} \cos \frac{r' \pi x}{l} dx = 0 \text{ if } r \neq r'$$

$$= \frac{l}{2} \text{ if } r = r'$$

and $\int_0^l \sin \frac{r \pi x}{l} \cos \frac{r' \pi x}{l} dx = 0$ in any event.

This wipes out a great body of terms, and it follows that only the squares of *individual* expressions such as are written within the brackets in (19.2.4), will yield finite amounts. Even in these we shall find in the end no products such as $\dot{q} \dot{q}'_1, \dot{q} \dot{q}'_2, \dot{q} \dot{q}'_3$, since in the case of such products we are involved in integrations such as

$$\int_0^l \int_0^l \int_0^l \sin r\phi \cos r\phi \sin s\psi \cos s\psi \sin u\chi \cos u\chi \, dx \, dy \, dz,$$

and these lead to a zero result. In the end a little inspection will show that the kinetic energy is the sum of

$$\frac{\rho l^3}{8} \{ (r^2 + s^2 + u^2) \dot{q}^2 + \dot{q}'_1^2 + \dot{q}'_2^2 + \dot{q}'_3^2 \}$$

over all the sets of values for r, s, u .

Turning now to the potential energy, we glance back at (19.1.4), which has to be multiplied by $dx\,dy\,dz$ and integrated throughout the body. The term $(\kappa + 4\mu/3)\theta^2$, in view of the remarks just made on the nature of the integrations, clearly only involves the squares of the q co-ordinates; the term $4\mu(\varpi_1^2 + \varpi_2^2 + \varpi_3^2)$ involves the squares of $(sq'_3 - uq'_2)$ and such like quantities. The quantity within the brackets $\{ \}$ in (19.1.4) looks as if it might give trouble. As a matter of fact, if the reader likes to take the trouble of working it out in detail, he will find that the integral of it vanishes, and if he shirks the task he can take the statement on faith. Still it looks as if the terms referred to in the previous sentence might give products; for they will yield on integration the sum of expressions such as

$$\frac{\pi^2 l}{8} \{ (sq'_3 - uq'_2)^2 + (uq'_1 - rq'_3)^2 + (rq'_2 - sq'_1)^2 \}$$

But the expression inside the bracket is equal to

$$\begin{aligned} & (r^2 + s^2 + u^2) (q'_1{}^2 + q'_2{}^2 + q'_3{}^2) - (rq'_1 + sq'_2 + uq'_3)^2 \\ &= (r^2 + s^2 + u^2) (q'_1{}^2 + q'_2{}^2 + q'_3{}^2), \end{aligned}$$

in view of (19.2.2). Thus the statement that the energy of the lattice involves only squared terms in the generalised co-ordinates and velocities is justified.

So we arrive finally at a conclusion much the same as in the previous chapter; a lattice such as we have described of volume l^3 , and subject to the defined boundary conditions, can be regarded a large complex molecule with $3f$ internal degrees of freedom which, as far as the energy expressions are concerned, is analogous to a molecule with a number of internal oscillators. In this analogous molecule, f of the oscillators have each one degree of freedom, and each one has a period belonging to the series determined by a law such as (19.2.7). That one for instance which corresponds as regards period to the integers r, s, u , has a direction of motion whose direction cosines are proportional to r, s, u . (See equation (19.2.3).) Carefully note that these remarks are not made concerning the atoms of the lattice, but about the oscillators of a hypothetical molecule whose energy

function is formally identical with the formula for the energy of the lattice. There are f other oscillators in the molecule which have each two degrees of freedom, and each one a period drawn from a series determined by (19.2.8). The one which corresponds to the integers r, s, u vibrates in a plane whose normal has direction cosines proportional to r, s, u . (See equation (19.2.2).)

19.4 The Statistics of a System of Cubical Lattices.—Conceive then a system of n such cubical lattices capable of interchanging energy one with another, *viâ*, for example, the medium of an assemblage of gas molecules. We can derive momenta for each q co-ordinate of the lattice by the usual differentiation of the kinetic energy partially with respect to each \dot{q} velocity; set up the usual machinery of a phase-diagram of $6f$ dimensions, partition the representative points, and count the complexions in each statistical state. Then introducing the hypothesis of quantum states, we arrive at the conclusion that in the most probable state the number of lattices in the system of lattices which are in a quantum state, defined by the condition that the action-integrals of pdq (each one integrated throughout one period of the particular q) shall be certain integral multiples of h , are proportional to

$$e^{-\mu\epsilon}$$

where ϵ is the energy of that state and is equal to

$$\sum_{r=1}^i \sum_{s=1}^i \sum_{u=1}^i \left\{ a_{rsu} h\nu_{rsu} + 2 b_{rsu} h\nu'_{rsu} \right\} \quad . \quad . \quad (19.4.1)$$

the a_{rsu}, b_{rsu} being the $2f$ quantum numbers of the particular quantum state considered. The factor 2 in the second term arises from the two degrees of freedom of one set of oscillators in the analogous molecule. The average energy of a lattice is obtained as usual by evaluating

$$\frac{\sum \epsilon e^{-\mu\epsilon}}{\sum e^{-\mu\epsilon}} \quad . \quad . \quad . \quad . \quad . \quad (19.4.2)$$

where the Σ in the numerator and denominator indicates a *multiple* summation for all values from 0 to ∞ of each one of the $2f$ quantum numbers a_{rsu}, b_{rsu} . The symbolism has

become somewhat cumbersome, and it will enable the reader to arrive at the result more easily if we temporarily simplify the notation and consider an expression such as

$$\frac{\sum_{a=0}^{\infty} \sum_{b=0}^{\infty} \sum_{c=0}^{\infty} \dots (ax + by + cz + \dots) e^{-\mu(ax+by+cz+\dots)}}{\sum_{a=0}^{\infty} \sum_{b=0}^{\infty} \sum_{c=0}^{\infty} \dots e^{-\mu(ax+by+cz+\dots)}}$$

The letters $x, y, z \dots$ replace for the moment the individual $h\nu$, while a, b, c, \dots replace the quantum numbers.

Now the denominator of this expression can, as a little thought will show, be factorised. It is equal to

$$\left(\sum_{a=0}^{\infty} e^{-a\mu x} \right) \left(\sum_{b=0}^{\infty} e^{-b\mu y} \right) \left(\sum_{c=0}^{\infty} e^{-c\mu z} \right) \dots$$

The numerator can first of all be separated into a number of expressions such as

$$x \sum_{a=0}^{\infty} \sum_{b=0}^{\infty} \sum_{c=0}^{\infty} \dots a e^{-\mu(ax+by+cz+\dots)}$$

and this part of the numerator can as before be factorised into

$$x \left(\sum_{a=0}^{\infty} a e^{-a\mu x} \right) \left(\sum_{b=0}^{\infty} e^{-b\mu y} \right) \left(\sum_{c=0}^{\infty} e^{-c\mu z} \right) \dots$$

When this part of the numerator is divided by the denominator the result is

$$\frac{x \sum_{a=0}^{\infty} a e^{-a\mu x}}{\sum_{a=0}^{\infty} e^{-a\mu x}}$$

and this is

$$\frac{x}{e^{\mu x} - 1}$$

(See section 14.3).

Thus we see that the original expression is equal to

$$\frac{x}{e^{\mu x} - 1} + \frac{y}{e^{\mu y} - 1} + \frac{z}{e^{\mu z} - 1} + \dots$$

In this way it can be established that the average energy of a lattice, viz. (19.4.2), is equal to

$$\sum_{r=1}^i \sum_{s=1}^i \sum_{u=1}^i \left\{ \frac{h\nu_{rsu}}{\exp(\mu h\nu_{rsu}) - 1} + 2 \frac{h\nu'_{rsu}}{\exp(\mu h\nu'_{rsu}) - 1} \right\} \quad (19.4.3).$$

We can convert (19.4.3) into a definite integral just as in previous cases. The natural frequencies of a lattice for the q co-ordinates, which are beneath a certain value ν are in number the same as the number of *positive* integers the sum of whose squares is equal to $(2 l\nu/c)^2$. (See equation (19.2.7).) This is the same as the number of points dotted at the corners of unit cubes inside one octant of a sphere whose radius is $2 l\nu/c$; and so it is just one-eighth of the volume of this sphere, *i.e.*,

$$\frac{\pi}{6} \left(\frac{2 l\nu}{c} \right)^3 \text{ or } \frac{4 \pi l^3 \nu^3}{3 c^3}.$$

Thus the number of frequencies which lie in a range of frequency ν to $\nu + \delta\nu$ is

$$\frac{4 \pi l^3}{c^3} \nu^2 \delta\nu,$$

and so we convert (19.4.2) into a definite integral by collecting terms which satisfy

$$\begin{aligned} \nu + \delta\nu &> \nu_{rsu} > \nu \\ \nu' + \delta\nu' &> \nu'_{rsu} > \nu' \end{aligned}$$

to supply one element of the integral giving each of these terms the value which corresponds to ν and ν' and multiplying by the number of terms, *viz.* $(4 \pi l^3/c^3) \nu^2 \delta\nu$ and $(4 \pi l^3/c^3) \nu'^2 \delta\nu'$. We can obviously in the final result drop the stroke over the ν' and write the average energy of the lattice of volume l^3 or V to be

$$V \left(\frac{1}{c^3} + \frac{2}{c'^3} \right) \frac{4 \pi h \nu^3}{e^{\mu h \nu} - 1} d\nu \quad . \quad . \quad (19.4.4).$$

19.5 Standing Waves.—The boundary conditions which were imposed so as to give a definite character to the problem in hand can be exhibited in another light. Reverting for a moment to the linear lattice, it will be observed that,

selecting any term from the series which expressed the displacement, say $a_r \sin r \pi x/l \cdot \cos \omega_r t$, it can be written

$$\frac{1}{2} a_r \sin \frac{r \pi}{l} (x - ct) + \frac{1}{2} a_r \sin \frac{r \pi}{l} (x + ct).$$

If we therefore considered an unlimited string and two *progressive* waves

$$\xi = \frac{1}{2} a_r \sin \frac{r \pi}{l} (x - ct)$$

and
$$\xi = \frac{1}{2} a_r \sin \frac{r \pi}{l} (x + ct)$$

passing along it, the first in the direction of x positive, the latter in the opposite direction, the result would be that the appearance of progression is absent. The string would behave as if it were divided into segments of length l , each segment vibrating as an individual in its r^{th} upper partial. We would have a group of "standing waves." Thus the most general vibration can be regarded as a composition of standing waves of different periods each wave being equivalent to the existence of two progressive waves of equal amplitude travelling in opposite directions.

The superficial lattice exhibits the same features. The expression for one harmonic of the complete vibration can be regarded as the sum of four progressive waves such as

$$\xi = \frac{1}{4} a_{rs} \cos \frac{\kappa \pi}{l} (ax + \beta y - ct)$$

$$\xi = \frac{1}{4} a_{rs} \cos \frac{\kappa \pi}{l} (ax + \beta y + ct)$$

$$\xi = \frac{1}{4} a_{rs} \cos \frac{\kappa \pi}{l} (ax - \beta y - ct)$$

$$\xi = -\frac{1}{4} a_{rs} \cos \frac{\kappa \pi}{l} (ax - \beta y + ct)$$

where

$$a = \frac{r}{(r^2 + s^2)^{\frac{1}{2}}}, \beta = \frac{s}{(r^2 + s^2)^{\frac{1}{2}}}$$

$$\kappa = (r^2 + s^2)^{\frac{1}{2}}.$$

The first two represent two oppositely propagated progressive waves, one in the direction (α, β) , one in direction $(-\alpha, -\beta)$; the second two represent waves in directions $(\alpha, -\beta)$ and $(-\alpha, \beta)$. All four have the same speed c . (Note that $\pm \alpha, \pm \beta$ are direction cosines.) Thus the lattice with fixed edges might be regarded as a part of an infinite lattice with four sets of widely-extended waves for each (r, s) harmonic travelling across its surface.

Taking now a special term from the complete expression for a cubical lattice, say

$$\begin{aligned}\xi &= r q_{rsu} \cos \frac{r \pi x}{l} \sin \frac{s \pi y}{l} \sin \frac{u \pi z}{l} \\ &= r a_{rsu} \cos \frac{r \pi x}{l} \sin \frac{s \pi y}{l} \sin \frac{u \pi z}{l} \cos \omega_{rsu} t\end{aligned}$$

it will be found that this can be regarded as the sum of eight progressive waves. (We drop the suffixes as unnecessary at the moment.)

$$\begin{aligned}\xi &= \frac{1}{8} ra \cos \frac{\kappa \pi}{l} \left(ax + \beta y + \gamma z - ct \right) \\ \xi &= \frac{1}{8} ra \cos \frac{\kappa \pi}{l} \left(ax + \beta y + \gamma z + ct \right) \\ \xi &= \frac{1}{8} ra \cos \frac{\kappa \pi}{l} \left(ax - \beta y - \gamma z - ct \right) \\ \xi &= \frac{1}{8} ra \cos \frac{\kappa \pi}{l} \left(ax - \beta y - \gamma z + ct \right) \\ \xi &= -\frac{1}{8} ra \cos \frac{\kappa \pi}{l} \left(ax + \beta y - \gamma z - ct \right) \\ \xi &= -\frac{1}{8} ra \cos \frac{\kappa \pi}{l} \left(ax + \beta y - \gamma z + ct \right) \\ \xi &= -\frac{1}{8} ra \cos \frac{\kappa \pi}{l} \left(ax - \beta y + \gamma z - ct \right) \\ \xi &= -\frac{1}{8} ra \cos \frac{\kappa \pi}{l} \left(ax - \beta y + \gamma z + ct \right)\end{aligned}$$

where

$$\alpha = \frac{r}{(r^2 + s^2 + u^2)^{\frac{1}{2}}}, \text{ etc.}$$

$$\kappa = (r^2 + s^2 + u^2)^{\frac{1}{2}}.$$

Each of these represents a progressive wave of amplitude $\frac{1}{8} ra$ and speed c travelling in one of the eight directions given by ringing the changes on the signs of the direction cosines $\pm \alpha, \pm \beta, \pm \gamma$. In the same way the vibration-component of η can be split up into progressive waves of amplitude $\frac{1}{8} sa$, having the same harmonic factors, and likewise for ζ . When we associate the whole twenty-four into eight sets of three, each trio of course involving ξ, η, ζ , it will be found that the resultant amplitude has the same direction as the corresponding direction cosines of the trio. In short, the waves are longitudinal. The transverse can be treated in a similar manner.

Now the special feature referred to at the beginning of this section is this: Taking a point o, y', z' on a face of the cube and the point l, y', z' on the opposite face directly opposing it, we see that for the longitudinal standing wave

$$\xi_{rsu} = \Sigma \Sigma \Sigma ra \cos r\phi \sin s\psi \sin u\chi \cos (\omega_{rsu} t - \epsilon_{rsu})$$

etc.

the displacement components η_{rsu}, ζ_{rsu} vanish while the individual harmonic constituents of ξ_{rsu} are

$$ra \sin \frac{s \pi y'}{l} \sin \frac{u \pi z'}{l} \cos \left(\omega_{rsu} t - \epsilon_{rsu} \right) \text{ at } o, y', z'$$

$$\pm ra \sin \frac{s \pi y'}{l} \sin \frac{u \pi z'}{l} \cos \left(\omega_{rsu} t - \epsilon_{rsu} \right) \text{ at } l, y', z'.$$

Each of these harmonic vibrations has the same amplitude $ra \sin (s \pi y'/l) \sin (u \pi z'/l)$, and is in the same or opposite phase. These remarks can be extended to the transverse waves.

Thus we find that the behaviour of the cubical lattice simulates that of a cubical portion of an infinitely extended lattice through which are travelling a specially selected group of progressive waves, one half longitudinal, one half transverse. These waves produce standing waves in such a manner that at points directly facing each other on two

parallel faces of the cube, the *normal* components of the longitudinal vibration are always in the same or opposite phases, while the components *in the surface* of transverse vibration have the same character.

The drawback of this analysis of the vibrations of a lattice (which is originally due to Jeans) for the problem in hand is that it really concerns a continuous medium. The number of components is really infinite, whereas for our purpose we have to cut the series off sharp in an artificial manner since we are thinking of a group of discrete particles. Nevertheless the quantum result (19.4.3) or (19.4.4) obtained from it, was used by Debye towards the close of the first period of quantum history to deal with the question of the specific heat of solids and its success was so marked that when a little later Born and Karman actually solved the difficult problem of the real periods of a lattice proper, the improvement in the agreement of calculation with observation was not so noticeable. Born and Karman's analysis is too long and difficult to reproduce here, but a reader with rather more than the usual run of mathematics at his command could consult Born's works, *Dynamik der Kristallgitter*, or *Theorie des Festen Zustanden*. As stated, the analysis for a continuous medium was made by Jeans in 1906 in connection with the problem of full radiation, following up an earlier hint of the late Lord Rayleigh's. The ether being regarded, in the familiar fashion of those days, as a continuous medium capable of propagating transverse vibrations alone, the energy of radiation in a volume l^3 of it could be determined by multiplying the average energy corresponding to a frequency by the number of natural frequencies in a range ν to $\nu + \delta\nu$, viz., $8\pi l^3 \nu^2 \delta\nu / c^3$,* where c is the velocity of light, and summing over all the frequencies. We have seen that statistical mechanics distributes the energy on the average between these frequencies in the same manner as it distributes it between the ordinary co-ordinates and momenta of a particle system, because the motion can be

* The number of longitudinal frequencies ($4\pi l^3 \nu^2 \delta\nu / c^3$) is zero since c for longitudinal vibrations in the ether is infinite, as this was considered to be an incompressible medium.

analysed in terms of specially chosen co-ordinates and momenta (in a wider sense), and to each co-ordinate there is one corresponding frequency. This procedure has, of course, still to be justified to the reader, but all in good time. If then we adopt classical views, we ascribe $k\theta$ to each frequency, and find for the energy per unit volume of full radiation in the ether ("full" in the sense that it is in statistical equilibrium with its surroundings)

$$\int_0^{\infty} \frac{8 \pi \nu^2 k\theta}{c^3} d\nu \quad . \quad . \quad . \quad (19.5.1).$$

This is the famous *Rayleigh-Jeans Law*. Apart from the difficulty that the integral is infinite in value if we actually go to the upper limit, as we strictly should do if we regard the ether as a continuous medium, it does not fit the experimental facts within any finite range of frequencies except when well down in the infra-red. It concentrates all the energy as it were in the upper frequencies. Even if we artificially reduce the upper limit from ∞ to the highest known frequencies (say γ rays), and so evade the difficulty just mentioned, it is clear that as between the relatively few (though on our normal ideas of counting, enormous) degrees of freedom say in a cubic inch of iron and the relatively great number in a cubic inch of ether, the energy in a state of equilibrium should nearly all be in the ether and the iron just a trifle above absolute zero. This was a serious difficulty for older views, even before experiments on the spectral distribution of energy in full radiation had reached such precision as to pronounce a definite verdict against (19.5.1) in detail. These difficulties disappear if we replace $k\theta$ by the quantum result for the average energy which is not the same for all frequencies, but diminishes with frequency in a marked way on account of the exponential term in the denominator. We then obtain for the energy-density of full radiation

$$\frac{8 \pi h}{c^3} \int_0^{\infty} \frac{\nu^3}{\exp(h\nu/k\theta) - 1} d\nu \quad . \quad . \quad . \quad (19.5.2).$$

This is Planck's famous expression, although he obtained it originally in a very different way (actually five or six years before Jean's analysis). Of course (19.5.2) is a particular case of (19.4.4) with the longitudinal velocity infinite and the transverse velocity (here written c) put equal to the velocity of light.

CHAPTER XX

THE SPECIFIC HEATS OF SOLID BODIES

20.1 Einstein's Theory for Monatomic Solids.—According to the classical statistical theory, the specific heat per gram-atom, or atomic heat, of all monatomic solids should be $3R$ (5.94 calories per degree) at all temperatures. This, by the way, is the atomic heat at constant volume while the specific heat which is usually measured is obtained under conditions of constant pressure and is somewhat larger than the former, the difference being given by the formula

$$s_p - s_v = \frac{\alpha^2}{\kappa} V\theta,$$

where α is the coefficient of thermal expansion, κ the isothermal compressibility, and V the atomic volume. The theoretical s_p will, of course, vary somewhat from substance to substance by reason of differences in atomic weight and thermal and elastic properties, but the values are round about 6.4. Some metals keep reasonably near to this at ordinary temperatures, *e.g.*, silver, copper, lead, aluminium and zinc. On the other hand, substances like boron, beryllium, silicon, carbon, have values much too small at ordinary temperatures; diamond, for example, has an atomic heat 0.75 at -50°C. , and in any case all the substances show a marked decrease of specific heat with falling temperature.

Einstein was the first to suggest that the explanation of these facts lay in an abandonment of the equipartition theorem. He illustrated his suggestion in a rough and ready way by treating each atom in a monatomic solid as a harmonic oscillator with a frequency ν and three degrees of freedom. Thus the heat energy of a solid with f atoms would be

$$\frac{3 f h \nu}{e^{\mu h \nu} - 1}$$

and the thermal capacity would be equal to the differential coefficient of this with respect to θ , *i.e.*, to

$$3fk \frac{x^2}{(e^x - 1)^2}$$

where

$$x = \mu h\nu = \frac{h\nu}{k\theta}.$$

This only approaches the classical value $3R$ as x approaches zero, or θ approaches infinity ; for

$$\frac{x^2}{(e^x - 1)^2} = \frac{1}{\left(1 + \frac{x}{2!} + \frac{x^2}{3!} + \dots\right)^2}.$$

On the other hand, the expression diminishes indefinitely as x increases to an infinite value, *i.e.*, as θ approaches zero.

About the same time several attempts were made to evade the difficulty along classical lines. These took the form of assuming that with falling temperature some of the degrees of freedom become "frozen-in," to use a picturesque phrase, *i.e.*, that certain linkages otherwise free, and permitting some relative movement of different parts, become completely rigid. The trouble about these suggestions lay in the fact that if this were the case, the bodies should be much more difficult to compress at low temperatures than at high, and this is not so. Further, some time later, Einstein was able to derive a value for his mean frequency ν in terms of the atomic weight, density and compressibility of the material, and it turned out to be of the right order of magnitude to suit his specific heat formula. To be sure his assumption of one mean frequency was bound to produce a formula not completely in line with the facts, although a decided improvement on Dulong and Petit's law. For one thing, experimental work inspired by his result soon discovered that his value for s_v fell far too rapidly with temperature, on account of the exponential term in the denominator. In 1912 Debye published a very long paper on the whole matter. The first part consists of an investigation of the natural frequencies of a solid continuum leading with the help of the

quantum theory to the results of the previous chapter. He then proceeds to apply them to a lattice for which the frequencies must have an upper limit. It is in this step that the weak spot of Debye's method lies, yet his final results constitute as great an advance beyond Einstein's formula as the latter was beyond the law of Dulong and Petit.

We saw in section (19.4) that the number of natural frequencies for a cube of volume V which lie in the range ν to $\nu + \delta\nu$ is

$$4 \pi V \left(\frac{1}{c^3} + \frac{2}{c'^3} \right) \nu^2 \delta\nu.$$

Hence, if ν_m is the upper limit, the integral of this expression from 0 to ν_m must be the whole number of frequencies, i.e., $3f$, where f is the number of atoms in volume V . Thus

$$3f = \frac{4 \pi V}{3} \left(\frac{1}{c^3} + \frac{2}{c'^3} \right) \nu_m^3$$

$$\text{or} \quad \nu_m = \left\{ \frac{9f}{4 \pi V (c^{-3} + 2 c'^{-3})} \right\}^{\frac{1}{3}} \quad (20.1.1)$$

and since c and c' depend on the density and elastic constants of the substance, ν_m is calculable in terms of these quantities. The heat energy of the body is by (19.4.4)

$$4 \pi V \left(c^{-3} + 2 c'^{-3} \right) \int_0^{\nu_m} \frac{h\nu^3}{e^{h\nu} - 1} d\nu$$

which is equal to

$$\begin{aligned} & \frac{9f}{\nu_m^3} \int_0^{\nu_m} \frac{h\nu^3}{e^{h\nu} - 1} d\nu \\ &= \frac{9fk\theta}{x_m^3} \int_0^{x_m} \frac{x^3}{e^x - 1} dx \quad (20.1.2) \end{aligned}$$

where we write x for $h\nu/k\theta$ and x_m for $h\nu_m/k\theta$. The integral is, of course, a function of x_m , say $\psi(x_m)$, so that the heat energy at the temperature θ is

$$9fk\theta \cdot \frac{\psi(x_m)}{x_m^3}.$$

The differential coefficient of this with respect to θ is the thermal capacity of f atoms. This coefficient is

$$\begin{aligned} & \frac{9fk}{x_m^3} \psi(x_m) - \frac{27fk\theta}{x_m^4} \psi(x_m) \frac{dx_m}{d\theta} + \frac{9fk\theta}{x_m^3} \cdot \frac{d\psi(x_m)}{dx_m} \cdot \frac{dx_m}{d\theta} \\ &= \left(\frac{9fk}{x_m^3} + \frac{27fk\theta}{x_m^4} \frac{h\nu_m}{k\theta^2} \right) \psi(x_m) - \frac{9fk\theta}{x_m^3} \cdot \frac{x_m^3}{e^{x_m}-1} \cdot \frac{h\nu_m}{k\theta^2} \\ &= \frac{36fk}{x_m^3} \int_0^{x_m} \frac{x^3}{e^x-1} dx - \frac{9fkx_m}{e^{x_m}-1} \cdot \cdot \cdot \cdot (20.1.3). \end{aligned}$$

The expression in (20.1.3) is a definite function of x_m . Thus Debye arrived at the conclusion, that the atomic heat for any monatomic solid is represented by a universal function of a pure number x_m which has a characteristic value for each solid at a given temperature. This number is the ratio of the quantum of energy for the maximum frequency of the solid to the average energy (kinetic + potential) at the temperature per degree of freedom on the equipartition law. Obviously $h\nu_m/k$ has the physical dimensions of temperature and if we call $h\nu_m/k$ the "characteristic temperature" of a solid whose maximum frequency is ν_m , then $x_m = \theta_c/\theta$, where θ_c is this characteristic temperature. Thus the atomic heat can be written according to Debye as $D(\theta_c/\theta)$, where $D(y)$ is a function of the variable y defined by

$$D(y) = \frac{36R}{y^3} \int_0^y \frac{x^3}{e^x-1} dx - \frac{9Ry}{e^y-1} \quad \cdot \cdot (20.1.4).$$

If y is large, the second term in (20.1.4) becomes negligible, and since it is known that

$$\int_0^\infty \frac{x^3}{e^x-1} dx = \frac{\pi^4}{15}$$

it follows that for large values of y , the function $D(y)$ approximates to

$$\frac{12 \pi^4 R}{5y^3}$$

Hence by (20.1.4) the value at low temperatures of s_θ is

$$\frac{12 \pi^4 R}{5 \theta_c^3} \cdot \theta^3$$

and so the specific heat varies as the cube of the temperature when it approaches absolute zero. This is in excellent agreement with the experimental facts. We would expect the approximations at low temperatures to be good ; for in such a condition all the energy practically resides in those periodic motions which have the very smallest frequencies possible to the structure. The wavelengths in the solid for such frequencies are then so much longer than the separation between molecules that the assumption of a continuous medium inherent in certain parts of Debye's reasoning is practically justified in such extreme conditions.

If on the other hand y is small enough to permit of the approximation, $e_y = 1 + y$, the function $D(y)$ approximates to

$$\frac{36R}{y^3} \int_0^y x^2 dx - 9R,$$

or $3R$, and so we find that the specific heat at high temperatures has $3R$ as a limit, as it should be.

The result (20 . 1 . 4) has been tested for about half-a-dozen metals in a very searching manner. There is an expansion of $(e^x - 1)^{-1}$ as a series of powers of x which is well known to the pure mathematician, and whose coefficients have been calculated by him as a matter of interest in other connections than the needs of physical science.* This fortunate circumstance enables $D(y)$ to be calculated with not too much trouble for values of y ranging from small magnitudes, such as 0.1 to 10 or 20, or inversely to infer a value of y from a value of $D(y)$. From the nature of the result if the specific heat of a solid A at a temperature θ is the same as that of a solid B at temperature θ' , then θ bears to the characteristic temperature of A the same ratio as θ' bears to the characteristic temperature of B. Thus from the experimental values of the specific heats of a solid we should find consistent values for its characteristic temperature. But (20 . 1 . 1) permits us to calculate ν_m , and therefore θ_c , which is $h\nu_m/k$, in terms of the speeds c and c' , i.e., in terms of the elastic constants of the solid. A comparison of the values

* See Chrystal's *Algebra*, Vol. II., Chap. XXVIII.

of θ_c determined by such diverse methods provides a very clear test for the general validity of the ideas involved in Debye's analysis. Here are some results. The values in Column I. are derived from specific heat data, those in II. from measurements of the elastic constants.

| | I. | II. |
|-----------------|------|------|
| Lead . . . | 95° | 73° |
| Cadmium . . . | 168° | 174° |
| Silver . . . | 215° | 214° |
| Copper . . . | 309° | 332° |
| Aluminium . . . | 396° | 402° |
| Iron . . . | 453° | 484° |

Since the atomic heat of a simple substance is $f(\theta/\theta_c)$, where f is the *same* function for all the substances and θ_c is a constant characteristic of each substance, it should be possible to represent the variation of the atomic heat at constant volume with temperature for all substances *on the same curve*, provided the atomic heats are plotted as ordinates and the values of θ/θ_c as abscissæ. Schrödinger has shown that with a suitable choice of θ_c for each substance this deduction is very thoroughly verified by experiment. For details the reader should consult *Heat and Thermodynamics*, by J. K. Roberts, Chap. VII.

Diamond offers a very interesting illustration of this theory. On account of its elastic properties and its small density the velocities c and c' in the formula (20 . 1 . 1) are exceptionally large. This means that the value of ν_m , and therefore of θ_c , is also exceptionally great. In fact, θ_c is 1,860. Thus the temperature of diamond should attain an abnormally high value before the value of its atomic heat comes anywhere near to the Dulong-Petit limit. This peculiar behaviour of diamond had been a puzzle to the physicist for many years until the Quantum theory cleared up the mystery.

CHAPTER XXI

THE ENTROPY CONSTANT OF A GAS

21.1 Nernst's Heat Theorem.—We are about to return to the question raised at the end of Chapter VII., concerning an absolute value for the entropy-constant of a gas, but postponed for further discussion until the modifications introduced into statistical-mechanical theory by quantum considerations had been explained. The matter is one which cannot be dissociated from the extremely valuable suggestion concerning entropy first made by Nernst in 1906; and no apology is therefore needed for a digression at this point into purely thermodynamic theory placing before the reader in general terms what that innovation amounted to.

In a chemical reaction or physical change which takes place *at constant volume and temperature*, there is a simple connection between the heat absorbed or evolved by the system and the change in its free energy. Choosing θ , v to represent the thermodynamic variables, temperature and volume, and $\alpha_1, \alpha_2, \dots$ to represent other variables which are involved in the reaction or change, let us denote the internal energy, free energy and entropy by the functional symbols

$$\begin{aligned} E(\theta, v, \alpha_1, \alpha_2, \dots), & \quad F(\theta, v, \alpha_1, \alpha_2, \dots), \\ S(\theta, v, \alpha_1, \alpha_2, \dots) & \end{aligned}$$

respectively. The amount of heat supplied to the system in an elementary change is given by

$$\delta Q = \frac{\partial E}{\partial \theta} \delta \theta + \frac{\partial E}{\partial v} \delta v + \sum \frac{\partial E}{\partial \alpha_r} \delta \alpha_r + p \delta v$$

where p is the pressure; p is, of course, a function of θ and v given by the characteristic equation of the system. Since $E = F + \theta S$, it follows that

$$\delta Q = \frac{\partial (F + \theta S)}{\partial \theta} \delta \theta + \frac{\partial (F + \theta S)}{\partial v} \delta v + \sum \frac{\partial (F + \theta S)}{\partial \alpha_r} \delta \alpha_r + p \delta v$$

and if the reaction or change occurs at constant temperature and volume, then

$$\begin{aligned}\delta Q &= \Sigma \frac{\partial F}{\partial a_r} \delta a_r + \theta \Sigma \frac{\partial S}{\partial a_r} \delta a_r \\ &= \Sigma \frac{\partial F}{\partial a_r} \delta a_r - \theta \Sigma \frac{\partial}{\partial a_r} \left(\frac{\partial F}{\partial \theta} \right) \delta a_r\end{aligned}$$

since $S = -\partial F/\partial \theta$. Thus we obtain

$$\delta Q = \Sigma \frac{\partial F}{\partial a_r} \delta a_r - \theta \frac{\partial}{\partial \theta} \left(\Sigma \frac{\partial F}{\partial a_r} \delta a_r \right).$$

Hence the heat absorbed by the system during a finite reaction or change occurring at constant volume and temperature in which the a_r variables vary in value from a'_r to a''_r , is given by the expression

$$\Sigma \int_{a'_r}^{a''_r} \frac{\partial F}{\partial a_r} da_r - \theta \frac{\partial}{\partial \theta} \left(\Sigma \int_{a'_r}^{a''_r} \frac{\partial F}{\partial a_r} da_r \right).$$

Since the first term in this expression is the change in the free energy, we have here the familiar equation of the textbooks on physical chemistry

$$U = A - \theta \frac{\partial A}{\partial \theta} \quad . \quad . \quad . \quad (21.1.1)$$

where U is the heat *evolved* during a reaction or change and A is the *loss* of free energy, $\partial A/\partial \theta$ being, of course, estimated at constant volume.

Now it is with the free energy that the physical chemist is vitally concerned. He can measure the quantity U , and so the simple differential equation (21.1.1) enables him to calculate the loss of free energy apart from an arbitrary constant of integration. There is no clue to the value of this constant on grounds of pure mathematics. Its value must be obtained as the result of a suitable physical hypothesis. Nernst suggested that trial should be made with the condition that $\partial A/\partial \theta$ diminishes in value to zero as a limit as the temperature approaches absolute zero, *i.e.*,

$$\frac{\partial A}{\partial \theta} \rightarrow 0 \text{ as } \theta \rightarrow 0. \quad . \quad . \quad . \quad (21.1.2).$$

The suggestion has been abundantly supported by experimental results,* and so the equation (21.1.2) is the mathematical form of Nernst's heat theorem, and by it is determined the "chemical constant" of any reaction and the ambiguity in the solution of (21.1.1) removed.

But from what just precedes, we can clearly write the condition (21.1.2) in the form

$$\frac{\partial F(\theta, v, \alpha'_1, \alpha'_2, \dots)}{\partial \theta} = \frac{\partial F(\theta, v, \alpha''_1, \alpha''_2, \dots)}{\partial \theta}$$

if $\theta = 0$; or

$$S(\theta, v, \alpha'_1, \alpha'_2, \dots) = S(\theta, v, \alpha''_1, \alpha''_2, \dots) \quad (21.1.3)$$

if $\theta = 0$. In words, the difference between the entropy of the system before and after a reaction gradually disappears as the temperature at which the reaction occurs is reduced to the absolute zero as a limit.

21.2 The Entropy-Constant and the Vapour-Pressure-Constant.—As we saw in Chapter VII. the entropy of a gram-molecule of a perfect gas containing one type of molecule is

$$s_p \log \theta - R \log p + \kappa \quad (21.2.1)$$

where κ is a constant of integration, which is of no importance in dealing with the change of entropy between two states of the gas, but assumes quite a new significance when Nernst's theorem is considered in connection with it. Thus let us assume that at high enough temperature the vapour of a liquid is in such a condition that (21.2.1) is a good enough approximation to its entropy at temperature θ . At the same temperature let $\phi(\theta)$ be the entropy of the liquid; then

$$\frac{d\phi(\theta)}{d\theta} = \frac{s}{\theta}$$

where s is the specific heat of the liquid. Of course in $\phi(\theta)$ must also occur an undetermined constant of integration;

* See *System of Physical Chemistry*, Vol. II., Chapter XIII.; W. C. McC. Lewis.

but this constant is clearly settled by the value we choose for κ in (21.2.1); for

$$\phi(\theta) + \frac{L}{\theta} = s_p \log \theta - R \log p + \kappa \quad . \quad . \quad (21.2.2)$$

since the two entropies must differ by L/θ , L being the heat of vaporisation.

Let us turn for a moment to the well-known thermodynamic relations which hold for the change of state from liquid to vapour, and which are associated with the name of Clapeyron. They are

$$\frac{dp}{d\theta} = \frac{L}{(v_1 - v_2)\theta} \quad . \quad . \quad . \quad (21.2.3)$$

$$\frac{dL}{d\theta} - \frac{L}{\theta} = s_1 - s_2 \quad . \quad . \quad . \quad (21.2.4)$$

In the second, s_1 is the specific heat of the *saturated* vapour. Now in the condition of saturation at temperature $\theta + \delta\theta$, let the pressure be $p + \delta p$, and the specific volume be $v_1 + \delta v_1$. Conceive the vapour to expand to a specific volume $v_1 + \delta v_1 + \delta'v_1$, so that its pressure is restored to the original value p , the temperature still being $\theta + \delta\theta$, so that the vapour is unsaturated. If the temperature be so high that the conditions approximate to those of an ideal gas, then by Boyle's law

$$(p + \delta p)(v_1 + \delta v_1) = p(v_1 + \delta v_1 + \delta'v_1),$$

or practically

$$v_1 \delta p = p \delta'v_1$$

Now from the definition of s_1 it follows that

$$s_p = s_1 + p \frac{\delta'v}{\delta\theta}.$$

Therefore

$$s_p = s_1 + v_1 \frac{\delta p}{\delta\theta}.$$

Since v_2 is small compared to v_1 , this can be practically written

$$\begin{aligned} s_p &= s_1 + (v_1 - v_2) \frac{dp}{d\theta} \\ &= s_1 + \frac{L}{\theta} \end{aligned} \quad \text{by (21.2.3).}$$

Hence the second of the relations above becomes

$$\frac{dL}{d\theta} = s_p - s \quad . \quad . \quad . \quad (21.2.5)$$

where s , the ordinary specific of the liquid can be regarded as practically equal to s_2 . Thus (21.2.5) can be regarded as valid at sufficiently high temperatures. But the first relation (21.2.3) can under these circumstances be written

$$\begin{aligned} \frac{dp}{d\theta} &= \frac{pL}{R\theta^2} \\ \text{or} \quad \frac{d \log p}{d\theta} &= \frac{L}{R\theta^2} \quad . \quad . \quad . \quad (21.2.6) \end{aligned}$$

To connect these two approximate results (21.2.5) and (21.2.6) with our previous considerations of entropy, we must integrate them. Thus (21.2.5) yields

$$L = L_0 + s_p \theta - \int_0^\theta s(x) dx,$$

where L_0 is a constant of integration which may be called the "latent heat at absolute zero" without necessarily implying any physical reality for a change of state actually at this temperature. Of course s_p is a constant approximately equal to $5R/2$, but s is a function of temperature. The integral on the right-hand side is quite definite, and is equal to the increase in energy-content of the liquid* between absolute zero and θ , this increase being the actual energy-content if we consider the energy-content to be *nil* at absolute zero. But in any case it is a definite function of θ , say $E(\theta)$, and it is implied that $E(0) = 0$. Thus

$$L = L_0 + s_p \theta - E(\theta) \quad . \quad . \quad . \quad (21.2.7)$$

* If the condensed system at zero is really a solid, no ambiguity arises. The energy-content then contains a constant term (the latent heat of fusion) in addition to the integral.

Turning to (21.2.6) we find

$$\frac{d \log p}{d\theta} = \frac{L_o + s_p \theta - E(\theta)}{R\theta^2}$$

$$\text{and so } \log p = -\frac{L_o}{R\theta} + \frac{s_p}{R} \log \theta - \frac{1}{R} \int_o^\theta \frac{E(x)}{x^2} dx + \gamma \quad (21.2.8)$$

where γ is a second constant of integration; for the moment we pass over the point as to the possibility of an indefinite quantity arising at the lower limit of the integral since $E(\theta)/\theta^2$ is apparently an indeterminate quantity when $\theta = o$. It follows that

$$s_p \log \theta - R \log p = \frac{L_o}{\theta} + \int_o^\theta \frac{E(x)}{x^2} dx - R\gamma$$

Hence by (21.2.2)

$$\phi(\theta) = \frac{L_o}{\theta} + \int_o^\theta \frac{E(x)}{x^2} dx + \kappa - R\gamma - \frac{L}{\theta}$$

which by (21.2.7)

$$= \int_o^\theta \frac{E(x)}{x^2} dx + \frac{E(\theta)}{\theta} + \kappa - s_p - R\gamma \quad (21.2.9).$$

We can now derive the value of the entropy of the condensed substance at the absolute zero of temperature. It is

$$\lim_{\theta=o} \frac{E(\theta)}{\theta} + \kappa - s_p - R\gamma$$

By definition the first term on the right-hand side is s_o where s_o is the specific heat of the condensed system at absolute zero*; thus

$$\phi(o) = \kappa - s_p - R\gamma + s_o.$$

We are now in a position to see the bearing of Nernst's theorem on this analysis. Cases arise in which several allotropic forms of the condensed solid or liquid exist. Each form will have its own individual values of energy-content, latent heat, etc., at a given temperature θ . Hence since p ,

* Of course, although $E(\theta)/\theta$ approaches a definite value as θ approaches zero, it does not follow that $E(\theta)/\theta^2$ does so; hence the possibility of ambiguity in the integral $\int_o^\theta E(x)/x^2 dx$.

the pressure of the vapour, depends only on θ , it might readily be inferred from (21.2.8) that the vapour-pressure constant γ would depend on the particular allotropic form. But any chemical reaction in which one form is converted into another would, according to Nernst's theorem, change the entropy by an amount which tends to zero as the temperature at which the reaction is carried out is reduced in value. This means that $\phi(o)$ is the same for all allotropic forms. Now experiments on the part of Nernst and his collaborators were gradually convincing them that in point of fact the specific heats of simple solids and liquids tend to zero as θ approaches zero. Accepting this as an experimental fact, it appeared that the common value for the entropy at zero of any of the various condensed forms is

$$\kappa - s_p - R\gamma. \quad . \quad . \quad . \quad (21.2.10).$$

Experiment was moreover indicating more than the simple fact that s or $dE(\theta)/d\theta$ tends to zero as θ approaches zero; it was suggesting that the approach towards the limit is so rapid that $E(\theta)/\theta^2$ also tends towards zero, thus making the integral in (21.2.8) a perfectly definite quantity without any indeterminateness arising at the lower limit. This is, of course, quite in keeping with the theoretical discussions of Einstein, Debye, etc., which, however, were historically later. That being so, γ has a definite value for each form of the condensed material. But by (21.2.10) $\kappa - R\gamma$ must be independent of the particular form, and since κ , whatever value it receives, is only dependent on the vapour, the constant γ is therefore the same for all the allotropic forms of the condensed material.

It was at this point that Planck stepped into the discussion. Thermodynamics, even with Nernst's theorem, was still unable to assign any value to (21.2.10), the value of the entropy at zero. The constant γ can, no doubt, be experimentally determined by applying (21.2.8) to vapour-pressure measurements, but, of course, the entropy-constant of the vapour, κ , is, on thermodynamic grounds alone, entirely undetermined. By applying the quantum hypothesis to the statistical-mechanical considerations of Chapter

VII., Planck pointed out that there was considerable support for the view that the value of the entropy at the zero of temperature tends to zero as a limit. If this were so, this meant that one must assign a definite value to the entropy-constant, κ , of a vapour or gas, *viz.*, $R\gamma + s_p$, where γ is the experimental vapour-pressure constant, and s_p the ideal specific heat at constant pressure. It remains to show how Planck was guided to this conclusion. His arguments were not regarded as quite convincing at first, and an extremely interesting discussion on the statistical-mechanical side of this matter went on for several years. We shall endeavour to summarise these investigations in the following chapter.

NOTE.—For the sake of the readers who are familiar with the *System of Physical Chemistry*, by W. C. McC. Lewis, it may be as well to point out that the γ of the text above is connected with the “characteristic constant” of the vapour, denoted in that work by the letter i , by the simple relation

$$\gamma = i + \log R.$$

For since

$$p = R C \theta,$$

where C is the concentration, it follows that

$$\begin{aligned} \log C &= -\frac{L_o}{R\theta} + \left(\frac{s_p}{R} - 1\right) \log \theta - \frac{1}{R} \int_0^\theta \frac{E(x)}{x^2} dx + \gamma - \log R \\ &= -\frac{L_o}{R\theta} + \alpha_o \log \theta + \frac{\beta_o}{R} \theta + \frac{\gamma_o}{2R} \theta^2 + \text{etc.}, + i \end{aligned}$$

which is the expression on page 76 of Vol. II. (2nd edition). The logarithms are, of course, to the Napierian base, e . The usual numerical values of the Nernst constant are determined on the understanding that 10 is the logarithmic base. In that case we must write the value for the logarithm of the vapour-pressure as follows

$$\log_{10} p = -\frac{L_o}{2.3023 R\theta} + \frac{s_p}{R} \log_{10} \theta - \frac{1}{2.3023 R} \int_0^\theta \frac{E(x)}{x^2} dx + c$$

where

$$c = \frac{\gamma}{2.3023} = \frac{i + \log R}{2.3023}.$$

CHAPTER XXII

THE ENTROPY CONSTANT OF A MONATOMIC GAS AND STATISTICAL MECHANICS

22.1 The Magnitude of the Phase-Cell.—The reader will recall certain remarks made at the beginning of Chapter XVI., in which was mentioned the question of adjusting probability calculations for a system whose particles may pass from a condition involving quantum paths to one in which the paths are not so restricted. No answer to such a problem can be evolved from purely mathematical *à priori* considerations; it is necessary to introduce a definite postulate and test its results by experiment. It was stated that one plausible hypothesis assigns even for a non-quantised state a fundamental size to the phase-cell depending on a suitable power of h ; in the case of particles with the usual three degrees of freedom for translatory motion it will be the third power. Now such a postulate naturally leads one to speculate if a similar specification of the size of the phase-cell may not prove convenient even when alternations between quantum and non-quantum conditions are not in question. In point of fact, very early in quantum history Planck introduced such considerations into the statistical treatment of a monatomic gas. We hinted as much in Chapter VII., where a symbol g was used *pro tem.* as indicating some definite magnitude having the dimensions of action cubed. There is certainly none of the obvious support for this view, which is supplied to the analogous hypothesis for internal vibratory motions where spectroscopy has provided such powerful aid. Nevertheless, discussion of this suggestion of Planck's proceeded apace, and, beginning with two rather famous papers by O. Sackur and H. Tetrode, a considerable volume of literature poured out dealing with this matter, gradually converging to the view that g

not only exists as a definite magnitude, but that its value is h^3 . Indeed, in some quarters attempts have been made to justify the postulate that even for the translatory motion of molecules in a gas system, quantisation of paths exists, and that experimental facts to support such a claim might be found at sufficiently high concentrations or at very low temperatures. In the former case the space available for molecular motion becomes restricted and molecular motion would have a zig-zag character which might be regarded as a vibration whose central point is gradually shifting. In the latter case the average molecular energy becomes very small. No very definite experimental results to prove such "degeneration of gases" are available, but it must be admitted that the conditions under which quantisation would become apparent would be very extreme, and it cannot be said that the claim is absolutely disproved as yet. The following rather artificial analysis shows how one might formally express this view. Regard the gas as enclosed in a cubical box of side l . Disregard intermolecular collisions and consider all collisions as between molecules and the sides. This is a kind of vibration on the part of each molecule with three degrees of freedom the amplitude for each degree being l . The action-integral for the component motion parallel to one edge (say the axis of x) is

$$2 \int_0^l m v_x dx,$$

which is equal to $2 m v_x l$, and similarly for the other components. Thus, corresponding to three integers r_1, r_2, r_3 , we would have a particular velocity of translation for a molecule given by the conditions

$$\begin{aligned} 2 m v_x l &= r_1 h \\ 2 m v_y l &= r_2 h \\ 2 m v_z l &= r_3 h, \end{aligned}$$

so that the energy of a molecule would have one of a series of discrete values such as

$$\frac{h^2}{8 m l^2} (r_1^2 + r_2^2 + r_3^2)$$

each value corresponding to a special choice of the integers r_1, r_2, r_3 .

Quite apart from these rather speculative considerations, indirect experimental evidence is available for choosing a definite size for a phase-cell even in the case of gases and putting it equal to h^3 . It exists in connection with the problem discussed in the last chapter.

Reverting to Chapter VII., it was shown that if the number of representative points in the respective phase-cells in the most probable state are denoted by $\nu_1, \nu_2, \nu_3, \dots \nu_c$, then

$$-\sum_{r=1}^c \nu_r \log \nu_r = n \left\{ \frac{5}{2} \log \theta - \log p + \log \frac{(2 \pi m k)^{\frac{3}{2}} k}{g} + \frac{3}{2} \right\}$$

(See equations (7.1.3) and (7.2.1)).

If W_m stands for the complexion-number of the most probable state, this means that if we adopt the suggestion for g

$$k (\log W_m - n \log n) = R \left\{ \frac{5}{2} \log \theta - \log p + \log \frac{(2 \pi m k)^{\frac{3}{2}} k}{h^3} + \frac{3}{2} \right\} \quad (22.1.1).$$

The reader will recall that in discussing the statistical basis of the second law of thermodynamics in Chapters VI. and XI., we selected the expression on the left-hand side of (22.1.1) as the entropy of a system. Nevertheless from the classical point of view it is clear that $k \log W_m \pm$ any constant would serve just as well. However, a reference to the conclusion of the last chapter will also remind him of Planck's suggestion that the entropy of a condensed system should be so chosen as to vanish at absolute zero. One necessary conclusion of this would be that the absolute entropy of any substance in this sense would be simply proportional to its amount. Thus the entropy of a quantity of gas would be proportional to n , and this consideration seems at once to justify the removal of $k n \log n$ from $k \log W_m$, as the expression on the right-hand side of (22.1.1) is certainly proportional to n . But a little reflection raises doubt once more since the further addition or subtraction of a multiple of n

(which is a constant) would still leave the expression for the entropy proportional to n . On reflecting still more, we are led to consider how the removal of $k n \log n$ arises in the analysis. It takes place when we write for W_m the expression

$$\frac{n^n}{\nu_1^{\nu_1} \nu_2^{\nu_2} \dots \nu_c^{\nu_c}}$$

and then divide W_m by n^n , so as to clear n out of the expression for "probability" and to obtain a logarithm of probability which is proportional to n . But the expression just written for W_m is an approximation; why not clear n out of the exact expression for W_m , viz.,

$$\frac{n!}{\nu_1! \nu_2! \dots \nu_c!}.$$

If we do so, we would choose for the entropy not $k \log (W_m/n^n)$ but $k \log (W_m/n!)$, i.e.,

$$k (\log W_m - n \log n + n).$$

Now this line of reasoning is manifestly weak; nevertheless it leads to a result which can be tested by experiment. The entropy now becomes

$$R \left\{ \frac{5}{2} \log \theta - \log p + \log \frac{(2 \pi m k)^3}{h^3} \frac{k}{2} + \frac{5}{2} \right\} \quad (22.1.2).$$

If this be so, then we have at once ascertained a value for, the entropy constant of the last chapter, viz.,

$$\kappa = R \log \frac{(2 \pi m k)^3}{h^3} \frac{k}{2} + \frac{5R}{2}$$

and from the conclusion there established that the vanishing of the entropy of the condensed system at absolute zero makes κ equal to $R\gamma + s_p$, we arrive at the equality

$$\gamma = \log \frac{(2 \pi m k)^3}{h^3} \frac{k}{2} \quad (22.1.3)$$

since $s_p = 5R/2$.

But γ is a vapour-constant which can be determined by experiment. In (21.2.8)

$$\int_0^{\theta} E(x)/x^2 \cdot dx$$

is an integral which can be calculated from specific heat measurements by the method of quadratures, or by the expansion of $E(\theta)$ as series of powers of θ whose coefficients can be obtained from the experimental data. Thus (21.2.8) can be used in conjunction with specific heat and vapour-pressure measurements to find γ . Equation (22.1.3) can be written

$$\gamma = \log \frac{(2\pi M)^{\frac{3}{2}} R^{\frac{5}{2}}}{n^4 h^3},$$

where M is the molecular weight of the gas, n the number of molecules in a gram-molecule of gas (6.06×10^{23}) and R is the gram-molecular gas constant (8.32×10^7). Thus

$$\gamma = \gamma_0 + 1.5 \log M \quad . \quad . \quad . \quad (22.1.4)$$

where

$$\begin{aligned} \gamma_0 &= \frac{3}{2} \log 2\pi + \frac{5}{2} \log R - 4 \log n - 3 \log h \\ &= 10.17. \end{aligned}$$

If we adopt the base 10 for the logarithms as is general in the actual calculation of Nernst's constants, we find that

$$\begin{aligned} c &= \frac{10.17}{2.3026} + 1.5 \log_{10} M \\ &= 4.41 + 1.5 \log_{10} M \quad . \quad . \quad . \quad (22.1.5). \end{aligned}$$

The experimental determination of c in the cases of hydrogen, mercury and argon give values approximating to 4.3, 4.4, 4.45, respectively for the constant term in (22.1.5). The reader will recall that at sufficiently low temperatures, hydrogen behaves as a monatomic gas.

Despite this *à posteriori* justification by experiment no one can feel that the initial argument for $k (\log W_m - n \log n + n)$ as the entropy in preference to many other expressions apparently as plausible is very satisfactory. It is round this point, rather than the choice of h^3 as the magnitude of the phase-cell, that the discussion has been most keen. Planck himself has been most persistent in endeavouring to justify the division of W_m by $n!$ by considerations involving no other state than that of gas. His latest views are given at some length in the fifth edition of his famous book *Theorie*

der Wärmestrahlung. Briefly they amount to a statement that if we "quantise" the movements of the molecules, it does not matter to which molecule we attach a particular set of values for the quantum numbers r_1, r_2, r_3 , and as there are $n!$ permutations of n points possible, division by $n!$ simply embodies this indifference as to the individuality of the molecule. Nevertheless many investigators regard such arguments as fundamentally weak and hold that only by considering some process in which the number of molecules in the gas can be varied, can we settle without ambiguity the dependence of the entropy expression on n . Such a process can be found in the sublimation of a gas from a solid state; we can regard the molecules in the solid as in quantum states without postulating quantum states for the gas. The following is a short sketch of a line of argument of this type due to O. Stern.

22.2 Stern's Treatment of the Entropy-Constant Problem.

—Stern's paper is lengthy and rather involved. It falls naturally into two parts. In one of these, the vapour equation (21.2.8) derived in the last chapter is adapted to suit the view that the internal energy $E(\theta)$ of the condensed part of the system is determined by quantum considerations; *i.e.*, thermodynamical reasoning goes into co-operation with the hypothesis that quantum states exist *in the condensed substance* (which is regarded as a cubical lattice such as we dealt with in Chapter XIX.), but no hypothesis that quantum states exist in the vapour is introduced. The result of this train of reasoning is the equation

$$\log p = - \frac{L_0 + \sum_{r=1}^{3f} h\nu_r}{R\theta} + \frac{5}{2} \log \theta + 3 \log \left(\frac{h\nu}{k\theta} \right) + \gamma \quad (22.2.1)$$

where $\nu_1, \nu_2, \dots, \nu_{3f}$ are the $3f$ natural periods of a lattice of f atoms as given by (19.2.7) and (19.2.8) and ν is their geometric mean—in other words

$$\nu^{3f} = \nu_1 \cdot \nu_2 \cdot \dots \cdot \nu_{3f} \quad (22.2.2)$$

R is written for fk .

The other part of the paper is the derivation by statistical-

mechanical methods of a vapour-pressure formula for a cubical lattice and its vapour in statistical equilibrium. In this part quantum considerations are not involved, since the temperature is regarded as high enough to permit of the use of classical statistics. In this part Stern finds that

$$\log p = -\frac{W}{R\theta} - \frac{1}{2} \log \theta + \log \frac{(2\pi m)^{\frac{3}{2}} \nu^3}{k^{\frac{1}{2}}} \quad (22.2.3)$$

In this, $W = fw$, where w is the work required to bring one atom from complete rest in the solid into the vapour. No constant of integration appears in this equation; the molecular model is definite, and so gives the absolute value of the vapour pressure. Thermodynamics, on the other hand, only gives $dp/d\theta$ or $d \log p/d\theta$; it is for this reason that a constant of integration appears in (21.2.8) and (22.2.1). A comparison of (22.2.1) and (22.2.3) now yields

$$W = L_o + \sum_{r=1}^{3f} \frac{h\nu_r}{2}$$

and the result which we are anxious to justify, viz.

$$\gamma = \log \frac{(2\pi m k)^{\frac{3}{2}} k}{h^3}.$$

We shall briefly outline the development of each part of the paper.

I.—*The Thermodynamical Part.* In (21.2.8) let us write for a lattice of f atoms

$$E(\theta) = \sum_{r=1}^{3f} \frac{h\nu_r}{e^{\mu h\nu_r} - 1},$$

where, as usual, $\mu = (k\theta)^{-1}$.

Our task is now to integrate

$$\sum_{r=1}^{3f} \frac{h\nu_r}{x^2 \{ \exp(h\nu_r/kx) - 1 \}} dx$$

from 0 to θ . Considering one term, we have

$$\begin{aligned} & \int_0^\theta \frac{h\nu_r/x^2}{\exp(h\nu_r/kx) - 1} dx \\ &= -k \int_{\infty}^{\eta} \frac{dy}{e^y - 1}, \end{aligned}$$

where $y = h\nu_r/kx$ and $\eta = h\nu_r/k\theta$. This is equal to

$$\begin{aligned} & k \int_{\eta}^{\infty} \left\{ \frac{e^y}{e^y - 1} - 1 \right\} dy \\ &= k \left[\log (e^y - 1) - y \right]_{y=\eta}^{y=\infty} \end{aligned}$$

At the upper limit, $y = \infty$, $\log (e^y - 1)$, is practically $\log e^y$ or y , and so the integral is equal to

$$\begin{aligned} & k\eta - k \log (e^{\eta} - 1) \\ &= \frac{h\nu}{\theta} - k \log (e^{\mu h\nu} - 1). \end{aligned}$$

Now

$$\begin{aligned} \log (e^{\mu h\nu} - 1) &= \log \left(\mu h\nu + \frac{1}{2!} \mu^2 h^2 \nu^2 + \frac{1}{3!} \mu^3 h^3 \nu^3 + \dots \right) \\ &= \log \mu h\nu + \log \left(1 + \frac{1}{2} \mu h\nu + \dots \right). \end{aligned}$$

If the temperature θ be sufficiently high, $\mu h\nu$ is small enough to allow this to be written

$$\log (e^{\mu h\nu} - 1) = \log \mu h\nu + \frac{1}{2} \mu h\nu.$$

Hence it follows that

$$\int_0^{\theta} \frac{E(x)}{x^2} dx = k \sum_{r=1}^{3f} \left(\frac{1}{2} \frac{h\nu_r}{k\theta} - \log \frac{h\nu_r}{k\theta} \right),$$

and thus equation (21.2.8) becomes

$$\begin{aligned} \log p &= -\frac{L_0}{R\theta} + \frac{5}{2} \log \theta + \frac{k}{R} \sum_{r=1}^{3f} \log \frac{h\nu_r}{k\theta} - \frac{\sum_{r=1}^{3f} h\nu_r}{2R\theta} \\ &= -\frac{L_0 + \sum_{r=1}^{3f} \frac{h\nu_r}{2}}{R\theta} + \frac{5}{2} \log \theta + 3 \log \frac{h\nu}{k\theta}, \end{aligned}$$

using (22.2.2) and remembering that $R = fk$. This establishes equation (22.2.1).

II. The Statistical-Mechanical Part.—The second part of Stern's paper will probably cause more trouble to follow, since Stern uses the statistical method associated with the name of Gibbs. This method will be explained in Chapter XXIV., but even at this stage it should not be beyond the power of the reader to grasp its essential idea. Indeed we have already come very near to its use in Chapters XVIII. and XIX. Recall the fact that we regarded a lattice-system of f atoms as a huge molecule and considered the statistics of a large number, n , of such systems in an enormous gaseous envelope at a given temperature—a "temperature-bath" in fact. Thus we were dealing essentially with a "Gibbs ensemble" (or assembly) of n molecular systems. It is this idea that we shall exploit still further here.

The system is made up of A atoms in an enclosure. Of these a atoms will be in a gaseous state, and f will be in a solid lattice formation, so that $A = a + f$, but, of course, a and f can vary individually. This system is to be regarded as the "huge molecule." An ensemble of these systems, n in number, is supposed to be in the temperature-bath at temperature θ . Thus the systems will exchange energy and each system will have a history or travel along a "path" in a phase-diagram which will involve the representation of $3A$ co-ordinates and $3A$ momenta. The system co-ordinates will be $x_1, y_1, z_1, \dots, x_a, y_a, z_a, q_1, q_2, q_3, \dots, q_{3f}$ where x_r, y_r, z_r are the Cartesian co-ordinates of the r^{th} molecule in the gas, and q_1, q_2, \dots, q_{3f} are $3f$ "normal" co-ordinates of the lattice, as explained in Chapter XIX. The momenta of the system are $\xi_1, \eta, \zeta_1, \dots, \xi_a, \eta_a, \zeta_a, p_1, p_2, \dots, p_{3f}$ where $\xi_r = m\dot{x}_r$, $\eta_r = m\dot{y}_r$, $\zeta_r = m\dot{z}_r$, and p_r is the differential coefficient with respect to \dot{q}_r of the kinetic energy of the lattice which was shown to be a quadratic function of the \dot{q}_r involving only squared terms. A phase of a system is defined by the assignment of definite values to $x_1, \dots, q_{3f}, \xi_1, \dots, p_{3f}$. An extension-in-phase of the system is defined by a statement that the phase of the system lies between $x_1, \dots, q_{3f}, \xi_1, \dots, p_{3f}$, and $x_1 + \delta x, \dots, q_{3f} + \delta q_{3f}, \xi_1 + \delta \xi_1, \dots, p_{3f} + \delta p_{3f}$.

Now the probability that a particular system out of the

great number n of these systems is in an elementary phase-extension, so defined, is

$$I \exp(-\mu E) \frac{\delta x_1 \dots \delta z_a, \delta q_1 \dots \delta q_{3f}}{\delta \xi_1 \dots \delta \zeta_a, \delta p_1 \dots \delta p_{3f}} \quad (22.2.4)$$

where I is some constant, and E is the energy of the system in the central phase of this extension which is practically

$$\frac{aw + \xi_1^2 + \eta_1^2 + \zeta_1^2 + \dots + \xi_a^2 + \eta_a^2 + \zeta_a^2}{2m} + \phi(q, p),$$

where $\phi(q, p)$ stands for the quadratic function which is equal to the sum of the kinetic and potential energies of the lattice, and w is the work required to bring a molecule at rest from the lattice into the gas.

Having settled these preliminaries, let us work out the probability that the system is in such a condition that a particular atoms are in the gas, and the remaining f particular atoms are in the lattice. It will be the sum of the probabilities (22.2.4) for all possible phases, i.e.,

$$I \int \dots \int \exp(-\mu E) dx_1 \dots dp_{3f} \quad (22.2.5)$$

over all phases.

Our immediate object must be to perform this integration. In the first place (22.2.5) splits into the product of two multiple integrals

$$I \int \dots \int \exp\left\{-\mu \left[aw + (\xi_1^2 + \dots + \zeta_a^2)/2m\right]\right\} dx_1 \dots dz_a d\xi_1 \dots d\zeta_a \quad (22.2.6)$$

and

$$\int \dots \int \exp\{-\mu \phi(q, p)\} dq_1 \dots dp_{3f} \quad (22.2.7)$$

$$\begin{aligned} \text{Since } \int_{-\infty}^{\infty} \exp\left\{-\mu \xi^2/2m\right\} d\xi &= \left(\frac{2m}{\mu}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} e^{-x^2} dx \\ &= \left(\frac{2m\pi}{\mu}\right)^{\frac{1}{2}} \\ &= (2\pi m k\theta)^{\frac{1}{2}} \end{aligned}$$

it follows that the expression (22.2.6) is equal to

$$I e^{-\mu aw} V^a (2\pi m k\theta)^{\frac{3a}{2}} \quad (22.2.8)$$

where V is the volume of the gas, which can practically be considered the volume of the enclosure.

To work out (22.2.7) does not require so much "grind" as one might imagine, if one refers back to certain expressions in Chapter XIX. If the reader will look at (19.1.4), (19.2.5), (19.2.6), (19.2.7), (19.2.8), and bear in mind the substance of section (19.3), he can, if he takes a little trouble, convince himself that the energy $\phi(q, p)$ of the lattice in a particular phase can be expressed in the form

$$\frac{1}{2} \{ \omega_1^2 q_1^2 + \dots + \omega_{3f}^2 q_{3f}^2 + p_1^2 + \dots + p_{3f}^2 \},$$

where $\omega_1, \dots, \omega_{3f}$ are the $3f$ natural pulsances of the lattice and we have supposed that the co-ordinates q_1, \dots, q_{3f} have been changed by a constant multiplier to such values that the coefficient of p_r^2 in the kinetic energy is half of unity. This makes the calculation of (22.2.7) fairly simple, for since

$$\int_{-\infty}^{\infty} \exp \left(-\frac{1}{2} \mu p^2 \right) dp = \left(\frac{2}{\mu} \right) \int_{-\infty}^{\infty} e^{-x^2} dx = (2 \pi k \theta)^{\frac{1}{2}}$$

$$\text{and } \int_{-\infty}^{\infty} \exp \left(-\frac{1}{2} \mu \omega^2 q^2 \right) dq = \frac{(2 \pi k \theta)^{\frac{1}{2}}}{\omega} *$$

it follows that the expression (22.2.7) is equal to

$$\begin{aligned} & \left[(2 \pi k \theta)^{\frac{1}{2}} \right]^{3f} \frac{[(2 \pi k \theta)^{\frac{1}{2}}]^{3f}}{\omega_1 \cdot \omega_2 \dots \omega_{3f}} \\ &= \frac{(2 \pi k \theta)^{3f}}{(2 \pi)^{3f} \nu_1 \cdot \nu_2 \dots \nu_{3f}} \\ &= \left(\frac{k \theta}{\nu} \right)^{3f} \dots \dots \dots (22.2.9) \end{aligned}$$

ν being the geometric mean of the $3f$ frequencies $\nu_1, \nu_2, \dots, \nu_{3f}$.

Combining (22.2.8) and (22.2.9), it would seem that the probability that the A molecules in the enclosure are so

* The integration is not actually from $q = -\infty$ to $q = +\infty$; but we have on several occasions used the same procedure, since the contribution to the integral of the range of q beyond the actual extremes is negligible.

situated that *a particular* molecules are in the vapour and *f particular* in the solid is

$$I e^{-\mu a w} V^a (2 \pi m k \theta)^{\frac{3a}{2}} \left(\frac{k \theta}{\nu} \right)^{3f}.$$

But in this conclusion we have overlooked one point. We have implicitly assumed that there are not only *f* particular molecules in the lattice, but that they are disposed in a particular way, each molecule oscillating about a particular position of equilibrium. With these *f* molecules we can make *f*! different arrangements out of any one which we have just considered, by permuting the molecules precisely as if they were *f* balls in *f* "pigeon-holes." It follows that the complexions are *f*! more numerous than we thought, and the probability for *a particular* molecules in the gas and *f particular* in the solid is

$$f! I e^{-\mu a w} V^a (2 \pi m k \theta)^{\frac{3a}{2}} \left(\frac{k \theta}{\nu} \right)^{3f}. \quad (22.2.10).$$

The last step in the probability calculation involves the removal of the epithet, "particular." There are $A!/a!f!$ ways of choosing *a* molecules to go in the gas and *f* in the solid; so the probability that there are *a* molecules (*any* molecules) in the gas and *f* in the solid is

$$\frac{A!}{a!} I e^{-\mu a w} V^a (2 \pi m k \theta)^{\frac{3a}{2}} \left(\frac{k \theta}{\nu} \right)^{3f}. \quad (22.2.11).$$

This is a function of *a* and *f* (really of *a* only, since *a* + *f* is constant) and our business is now to find when it is a maximum, as this will give us the most probable distribution of the molecules between gas and solid, *i.e.*, the distribution which we will meet in experiment. To find this, we put the differential coefficient of the expression (22.2.11) with respect to *a* equal to zero—or rather more easily, the differential coefficient of the logarithm of it. Thus we find

$$\begin{aligned} -\frac{d}{da} \log a! - \mu w + \log V + \frac{3}{2} \log (2 \pi m k \theta) \\ - 3 \log k \theta + 3 \log \nu = 0 \end{aligned}$$

(remember that $df/da = -1$). Putting $\log a!$ equal to $a \log a - a$, we find

$$-\log a + \log V - \frac{w}{k\theta} + \frac{3}{2} \log \left(\frac{2\pi m}{k\theta} \right) + 3 \log \nu = 0.$$

But the pressure in the gas is given by

$$p = \frac{a}{V} k \theta,$$

so that

$$\begin{aligned} \log p &= \log a - \log V + \log (k \theta) \\ &= -\frac{w}{k\theta} + \frac{3}{2} \log (2\pi m) - \frac{1}{2} \log k \theta + 3 \log \nu, \end{aligned}$$

which is just (22.2.3).

CHAPTER XXIII

ENSEMBLES OF SYSTEMS. I

23.1 The Probability Postulate and Dynamics.—Throughout all the reasoning so far has run the implicit assumption that the probability of the occurrence of a particular state of a system is proportional to the number of complexions embraced in that system. It now behoves us to turn our attention to any justification which can be found for this postulate. As we pointed out in an earlier passage, the complexions of a system can hardly be said to follow one another in the same manner as the complexions of a group of coins or dice follow one another in the chance of the cast. In short, we have to see what dynamical principles have to say in this matter. When it comes down to “brass tacks,” the reader may as well realise at once that we are on very doubtful ground indeed if we insist on rigorous logic unless we abandon the attempt to be definite about *one* system only and enlarge our field of view to embrace the lives of many systems each having the same dynamical character, but each having its own individual history which is distinct from those of its fellows.

Paradoxically enough, if we attempt a similar enlargement in the case of coin-tossing or dice-throwing, we are entirely in the dark experimentally. Many people have tossed pennies and found that out of a long *succession* of attempts, practically half are heads and half tails; but the author is not aware of any occurrence in which several thousand people threw pennies in the air simultaneously and observed the distribution of heads and tails at each throw. Indeed, we should have to imagine such a crowd of people each tossing several dozen pennies and observing how far the proportionality of probability to complexion-number is obeyed when the complexion of each system of pennies is

recorded and the facts for the "ensemble" or assembly of the systems compiled. Yet if instead of dealing with one dynamical system we consider an ensemble of systems, we are on very firm ground experimentally and we proceed to show why.

We shall begin with a very simple system indeed—our old friend, the uniformly accelerated falling particle; it is a system with one degree of freedom; *i.e.*, its position is given by one co-ordinate, *viz.*, the distance below some definite level. But we want to consider an ensemble of these systems; so we shall visualise a shower of rain—with the resisting air conveniently removed—and arrange that each drop has its own line of fall with no drop exactly in a vertical line with another. Under these circumstances many drops may at one moment be at the same level, *i.e.*, have the same value of the co-ordinate, which we shall denote by q , but we must conceive that they have not all the same value of velocity or \dot{q} (\dot{q} is written for dq/dt); in other words, these drops have fallen from different heights at such instants as to place them now (but not before or after) at the same level. Look at this another way; we know from dynamical theory that

$$q = a + bt + \frac{1}{2}gt^2 (23.1.1)$$

In this equation a and b are constants of integration; their values are arbitrary; they vary from particle to particle and give an individuality to each member of the ensemble. But g is common to all members. It is determined by the field of gravity—*i.e.*, the external bodies acting on each system affects them all alike. We call it a "parameter" of the system. It is obviously possible to choose many sets of values of a and b which give the same value of $a + bt$ for a *given* value of t ; the particles involved will all have the same value of q at the time t . But since

$$\dot{q} = b + gt (23.1.2)$$

and since b is not the same for this group of particles, their velocities are different at this level. In this way we arrange that no two particles have the same *phase* at any given moment, phase depending on both position and velocity.

Suppose then we represent this state of affairs on a phase-diagram. We shall draw as usual two rectangular axes, OX, OY, and represent the phase of each system at a definite instant by a point P, the x co-ordinate being equal to q , the y co-ordinate being equal to the momentum, $m\dot{q}$. As the system moves, *i.e.*, as the drop falls, the phase-point P moves along a stretch of a parabola in the phase-diagram; this is the "path" or "trajectory" of the representative point. This point has a velocity in the phase-diagram, whose components parallel to OX and OY are \dot{q} and \dot{p} respectively. For the moment denote these by u and v , so that $u = \dot{q}$, $v = \dot{p}$.

Now it is not difficult to express u and v as functions of x and y . Thus the energy of any system of the ensemble is equal to

$$\frac{1}{2} m \dot{q}^2 + mg (q_0 - q),$$

where q_0 is a constant (the same for all systems of the ensemble). This can be written

$$\frac{1}{2m} \cdot p^2 + mg (q_0 - q) \quad . \quad . \quad (23.1.3).$$

Represent this function by $E(q, p)$. It is easily seen from (23.1.2) that

$$\begin{aligned} \dot{q} &= \frac{\partial E(q, p)}{\partial p} \\ \dot{p} &= - \frac{\partial E(q, p)}{\partial q}, \end{aligned}$$

or

$$\begin{aligned} u &= \frac{\partial E(x, y)}{\partial y} \quad . \quad . \quad . \quad (23.1.4) \\ v &= - \frac{\partial E(x, y)}{\partial x}. \end{aligned}$$

But since

$$\frac{\partial u}{\partial x} = \frac{\partial^2 E(x, y)}{\partial x \partial y}$$

and

$$\frac{\partial v}{\partial y} = - \frac{\partial^2 E(x, y)}{\partial y \partial x},$$

it follows that

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad . \quad . \quad . \quad (23.1.5)$$

This simple relation embodies a result of supreme importance in our statistical considerations. Since we are considering an ensemble of systems, the phase-diagram will be covered with a crowd of points or dots, each one moving along one member of a family of parabolas. We can conceive the drops of rain to be so numerous and so many phases to be represented that the representative points are at any moment closely packed together in the phase-diagram, forming what is practically a dense "cloud" of points similar to a two-dimensional continuous fluid, and, of course, as the drops fall the cloud moves in the phase-diagram. Imagine that any moment the cloud fills a portion of the phase-diagram within some closed geometrical curve. Later its position has changed; it occupies a different region within another curve, most likely of different shape, but *the second region has the same area as the first*; that is the vital point. As each system of the ensemble passes through its successive positions and momenta, the cloud of representative points moves about on the phase-diagram, always occupying the same extension-in-phase. To prove this, all we require is equation (23.1.5). This, and, of course, a corresponding wider theorem, for systems with many degrees of freedom, is the great contribution of theoretical dynamics to statistical mechanics. Its implications we shall elicit presently. The proof for the simple one-degree system is not particularly troublesome.

Thus conceive an elementary rectangle of area $\delta x \delta y$ in the phase-diagram whose centre is at the point (x, y) , and let us calculate the net number of representative points of the cloud which move into the rectangle in time δt , which elapses after a certain instant denoted by t . At that instant there will be a definite distribution of density over the phase-diagram for the R-points.* We shall denote it by ρ , where, however, we must observe that this density is a function of x, y and t , and should really be symbolised by

* We must distinguish between points in the phase-diagram in the ordinary sense and *representative* points which are conceived to have a kind of substantiality and to move about. To signalise this we shall call the latter "R-points."

a functional form, such as $f(x, y, t)$; for we are not assuming that the R-points are uniformly distributed at any definite instant, not even over the area in which we considered them to be originally placed; nor do we assume that the density remains unchanged at a definite point of the phase-diagram throughout all time. It should also be remembered that u and v are functions of x and y also, and should be written $\phi(x, y)$, $\psi(x, y)$.* (Sec (23.1.4).)

Consider that side δy of the elementary rectangle which is nearest to the axis OY. Taking the value of u at its mid-point $(x - \frac{1}{2} \delta x, y)$, we see that the number of R-points which cross this side into the rectangle in time δt will at the instant t lie in a parallelogram whose side is δy , and height $\delta t \cdot \phi(x - \frac{1}{2} \delta x, y)$; for, of course, the component v of the velocity contributes nothing towards transport across a line parallel to OY. We can conceive δt to be so small that this height is small compared to δy , and so the density of the points in it at the instant t can be taken to be $f(x - \frac{1}{2} \delta x, y, t)$. Thus the number of R-points entering the rectangle by this δy side in time δt , is

$$\delta y f(x - \frac{1}{2} \delta x, y, t) \delta t \phi(x - \frac{1}{2} \delta x, y) \quad . \quad (23.1.6)$$

Similarly the number which leave the rectangle across the opposite δy side in time δt is

$$\delta y f(x + \frac{1}{2} \delta x, y, t) \delta t \phi(x + \frac{1}{2} \delta x, y) \quad . \quad (23.1.7)$$

In precisely the same manner the number which enter and leave the rectangle by the lower and upper δx sides respectively, are

$$\begin{aligned} & \delta x f(x, y - \frac{1}{2} \delta y, t) \delta t \psi(x, y - \frac{1}{2} \delta y) \\ & \delta x f(x, y + \frac{1}{2} \delta y, t) \delta t \psi(x, y + \frac{1}{2} \delta y) \quad . \quad (23.1.8) \end{aligned}$$

The mathematician is prone to lifting his eyebrows at this point, and, when it comes to mathematical rigor, he is justified in expressing doubt about our procedure; but life is short, and, in this book at all events, we cannot enter into all the mathematical niceties of proof. The reader can rest assured that the procedure can be justified if certain restric-

* In general dynamical reasoning u and v may also involve t ; but we are excluding cases where the "geometrical co-ordinates involve the time."

tions as to continuity and finiteness are imposed on the functions involved—restrictions which we believe are obeyed in these applications. The place where the ice is thin is the implicit assumption that, for example, $\phi(x - \frac{1}{2}\delta x, y)$ will practically serve as the expression for the velocity at any point on the left-hand side δy of the rectangle.

Gathering together results (23.1.6), (23.1.7) and (23.1.8), we obtain for the net *loss* of R-points in time from the rectangle

$$\delta y \frac{\partial}{\partial x} \{ f(x, y, t) \phi(x, y) \} \delta x \delta t + \delta x \frac{\partial}{\partial y} \{ f(x, y, t) \psi(x, y) \} \delta y \delta t$$

or briefly

$$\left\{ \frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} \right\} \delta x \delta y \delta t \quad . \quad . \quad (23.1.9)$$

But after time δt the density of the R-points at the point (x, y) becomes

$$f(x, y, t) + \frac{\partial}{\partial t} f(x, y, t) \delta t.$$

Thus the net *gain* of R-points in the rectangle is

$$\frac{\partial f(x, y, t)}{\partial t} \delta t \delta x \delta y,$$

$$\text{or} \quad \frac{\partial \rho}{\partial t} \delta t \delta x \delta y \quad . \quad . \quad . \quad (23.1.10)$$

Since results (23.1.9) and (23.1.10) must be consistent, it follows that

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} = 0.$$

Another simple step leads to

$$\frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} + v \frac{\partial \rho}{\partial y} + \rho \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) = 0 \quad . \quad (23.1.11)$$

This is the “equation of continuity,” which must be satisfied since raindrops are not being created or destroyed. But as u and v satisfy (23.1.5), we conclude that

$$\frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} + v \frac{\partial \rho}{\partial y} = 0 \quad . \quad . \quad (23.1.12)$$

This is the result of combining continuity with dynamical law.

After time δt , the R-point which was at the point (x, y) , has arrived at the point $(x + u \delta t, y + v \delta t)$, and the density of the R-points around it is

$$f(x + u \delta t, y + v \delta t, t + \delta t)$$

i.e.,

$$f(x, y, t) + \frac{\partial f(x, y, t)}{\partial x} u \delta t + \frac{\partial f(x, y, t)}{\partial y} v \delta t + \frac{\partial f(x, y, t)}{\partial t} \delta t,$$

or
$$\rho + \left(u \frac{\partial \rho}{\partial x} + v \frac{\partial \rho}{\partial y} + \frac{\partial \rho}{\partial t} \right) \delta t,$$

which by (23.1.12) is simply ρ . Thus as the cloud of R-points moves about in the phase-diagram, in a manner entirely determined by the *dynamical* behaviour of each member of the ensemble of systems, the density around any given R-point (*i.e.*, representative of a given drop of the ensemble), remains unchanged. Looked at in another way, this means that each element of area containing a definite number of R-points does not vary in size, and so this must also be true for finite stretches of the phase-diagram. The reader is warned that the proof does not concern the density around any given point of the phase-diagram; *i.e.*, it is not proved that $f(x, y, t + \delta t)$ is the same as $f(x, y, t)$, or that $\partial \rho / \partial t$ is zero. Put it in the language of Gibbs, we prove that "in an ensemble of mechanical systems identical in nature and subject to forces determined by identical laws, but distributed in phase in any continuous manner, the density-in-phase is constant in time for the varying phases of a moving system; provided that the forces of a system are functions of its co-ordinates." In this the emphasis is on the phrase "varying phases of a moving system"; the proposition is not necessarily true for the density around a *constant* phase.

To be sure our proof so far has been limited to systems with one degree of freedom; then we can appeal to our powers of visualisation to assist the understanding. That

the proof is general enough to cover *any* system with one degree of freedom (and not merely the falling particle) *provided the force is a function of the co-ordinate*, requires a very little adaptation at the beginning, which will be appreciated presently when we take the case of more complex systems. But before passing on it will be instructive to consider another simple system, *viz.*, the pendulum, since it illustrates very clearly a point which is of prime importance in the statistical applications.

In the ensemble of pendula all members have identical lengths, and swing in places with a definite value of g . In fact l and g are parameters. But the amplitude is an arbitrary constant introduced in integration of the equations of motion, and varies from member to member of the ensemble. The second arbitrary constant is the "epoch-angle" which settles at what instants the string is in a definite position, say the vertical. Further—and this is important—the periodic time is not the same for different amplitudes. The elementary theory of the pendulum, which brings out the value $2\pi (l/g)^{\frac{1}{2}}$ for this, considers only infinitesimal swings. The true result is $2\pi (l/g)^{\frac{1}{2}} f(a)$, where $f(a)$ is a function of the amplitude a concerning which all we need to specify at this moment is that it approaches unity as a approaches zero, but increases in value with a increasing. The angular co-ordinate, θ , and the angular momentum $ml^2\dot{\theta}$ will be represented in the phase-diagram. The R-point of any system will travel round a closed oval curve with O as centre—these ovals will approximate to elliptical form for small axes—but the time of making a complete circuit increases somewhat as the ovals increase in size. Take two points, P, Q, on one of these ovals and draw normals at them, cutting another oval outside and near it in points P', Q'. The figure P Q Q' P' is quasi-rectangular. Conceive a cloud of R-points distributed uniformly throughout it. As the corresponding systems in the ensemble oscillate in accordance with dynamical law, the R-points travel round the appropriate ovals. All those on one oval go round in the same time, but those on a given oval take a little longer than those on one within it. Thus

after one period for those on PQ, those originally on P'Q' have not quite arrived back, and similarly for those between PQ and P'Q'; there is a progressive lag as we go outwards. So the shape of "cloud-covered" patch is gradually more and more distorted from the initial "quasi-rectangularity" into a quasi-parallelogram shape, *but the area remains unchanged*. After some time the inner R-points will have overtaken the outer, and so the area is stretched like a spiral ribbon round between the inner and outer ovals. Still later we can have a very thin ribbon indeed spiralling many times round O as we go along it from inner to outer ends. Actually if the R-points were visualised as black dots on white paper, the whole space between the two ovals would present the appearance of blackness all over, or rather a continuous grey; and so if P Q Q' P' were an area equal to $1/n$ of the ring between the ovals it might appear that the R-points had now a uniform density equal to $1/n$ of the original; yet this is quite wrong in reality. Density, remember, is regarded as a function of x, y, t ; it is obtained by dividing a number of R-points in an element of area by the value of that area and proceeding to a limit. If we conceive this element of area to be in motion with the central R-point of it, we preserve unvarying density. If we conceive the element to be fixed, it is alternately empty and full of points. In other words, as time goes on the "black ribbon" grows longer and thinner, but the "white ribbon" in between does the same and maintains its size also. The sizes of the two parts maintain the same ratio, but of course the R-points are not so compactly situated as at the beginning, giving the impression of a uniformity of distribution over the whole annulus between the ovals which is an illusion. This reference to such an ensemble will help us in certain statistical considerations which will arise shortly.

23.2 Systems with Two Degrees of Freedom.—As the simplest illustration of this type, let us consider a particle moving in a plane in a field of force due to a centre of attraction or repulsion at an origin, and choose polar co-ordinates r and θ . Anyone with some knowledge of the

dynamics of a particle knows that the equations of motion are

$$m(\ddot{r} - r\dot{\theta}^2) = F$$

$$m \frac{d}{dt}(r^2\dot{\theta}) = 0$$

where F is the force directed from the centre. Now the kinetic energy is $\frac{1}{2} m(\dot{r}^2 + r^2\dot{\theta}^2)$ and the potential energy $V(r)$ where $F = -dV/dr$. The total energy is

$$\frac{1}{2} m(\dot{r}^2 + r^2\dot{\theta}^2) + V(r).$$

The partial differential coefficients of this with regard to \dot{r} and $\dot{\theta}$ respectively are $m\dot{r}$ and $mr^2\dot{\theta}$; these are the "momenta" in the general sense used throughout this book—they happen to be the ordinary linear momentum of the particle resolved along r , and the angular momentum round the centre. Call them p_r and p_θ . It easily follows that the energy is equal to

$$\frac{1}{2m} p_r^2 + \frac{1}{2mr^2} p_\theta^2 + V(r) \quad . \quad . \quad (23.2.1)$$

and it requires no great trouble to establish that the equations of motion above are equivalent to

$$\frac{dp_r}{dt} = - \frac{\partial E(r, \theta, p_r, p_\theta)}{\partial r} \quad . \quad . \quad (23.2.2)$$

$$\frac{dp_\theta}{dt} = - \frac{\partial E(r, \theta, p_r, p_\theta)}{\partial \theta} \quad *$$

where $E(r, \theta, p_r, p_\theta)$ is written for (23.2.1).

It can also be seen without much effort that

$$\frac{dr}{dt} = \frac{\partial E(r, \theta, p_r, p_\theta)}{\partial p_r} \quad . \quad . \quad (23.2.3)$$

$$\frac{d\theta}{dt} = \frac{\partial E(r, \theta, p_r, p_\theta)}{\partial p_\theta}$$

* It happens that the function E does not contain θ explicitly, and so $\partial E/\partial \theta$ is zero, but this accident does not invalidate the generality of the reasoning.

In fact, (23.2.2) and (23.2.3) constitute Hamilton's form for the equations of motion.

Conceive now the possibility of a representation in a four-dimensional phase-diagram, with r and θ represented along axes OX_1 , OX_2 and p_r and p_θ along axes OY_1 , OY_2 , so that if we denote the components of velocity of an R-point, representing some system, along its path in the diagram by u_1 , u_2 , v_1 , v_2 , where $u_1 = \dot{r}$, $u_2 = \dot{\theta}$, $v_1 = \dot{p}_r$, $v_2 = \dot{p}_\theta$ we have

$$\begin{aligned}u_1 &= \frac{\partial E(x_1, x_2, y_1, y_2)}{\partial y_1} \\u_2 &= \frac{\partial E(x_1, x_2, y_1, y_2)}{\partial y_2} \\v_1 &= -\frac{\partial E(x_1, x_2, y_1, y_2)}{\partial x_1} \\v_2 &= -\frac{\partial E(x_1, x_2, y_1, y_2)}{\partial x_2}\end{aligned}$$

From this it follows that

$$\frac{\partial u_1}{\partial x_1} + \frac{\partial u_2}{\partial x_2} + \frac{\partial v_1}{\partial y_1} + \frac{\partial v_2}{\partial y_2} = 0 \quad . \quad . \quad (23.2.4).$$

which corresponds to (23.1.5) and leads to similar conclusions; but more of this presently.

23.3 A Rigid Body.—This will briefly illustrate a system with six degrees of freedom. Three of these are easily disposed of; they correspond to the three ordinary co-ordinates of a point fixed in the body, say its centre of mass. The other three are a little troublesome to visualise; the reader will be helped by considering the earth in relation to the plane of the ecliptic and the fixed stars. These latter give us a "system of reference," *viz.*, the plane and some definite direction in it, say from sun to a definite point in one of the constellations of the Zodiac. As regards the earth we choose a convenient plane in it, and some definite direction in that plane, say the plane of the equator and a line from the centre to the point on the equator with longitude zero. Now the plane of the equator at any moment

intersects the plane of the ecliptic in a line, *viz.*, the “nodal” line, and there is a definite angle between the planes, the “inclination.” This angle constitutes one co-ordinate; in the case of the earth it remains nearly constant in time, only experiencing a secular periodic variation—the “nutation” of the earth’s axis. Then the nodal line makes with the line of reference to the constellation point (they both lie in the plane of the ecliptic) a definite angle, which is a second co-ordinate; in the case of the earth there is a slow increase of this angle at the rate of about one revolution in 27,000 years—the “precession” of the earth’s axis. Lastly, the nodal line makes a definite angle with the line on the earth from centre to zero longitude on the equator. In the case of the earth this third co-ordinate varies by 360° in one sidereal day. This method of choosing the “Eulerian angles” can be applied to any rigid body in a given frame of reference. Works on dynamics show how the kinetic energy can be expressed as a homogeneous quadratic function of $\dot{x}, \dot{y}, \dot{z}, \dot{\theta}, \dot{\phi}, \dot{\psi}$, where θ, ϕ, ψ are these angles. One important feature is that the coefficients of the individual terms may involve functions of the angles, such as $\cos\theta, \sin\theta, \sin\phi$, etc.; but we noticed that in the previous example a coefficient of a squared velocity term might involve a function of the co-ordinates (*e.g.*, $mr^2\theta^2$). Another feature is that product terms in the velocities as well as squared terms make their appearance.

CHAPTER XXIV

ENSEMBLES OF SYSTEMS. II

24 . 1 Hamilton's Equations.—In considering more complex systems than in the previous chapter, we can realise that the complete configuration of a system will be given by a suitable number of co-ordinates. Three of these would specify the position in a reference frame of some definite point of the system, say its centre of mass. For each particle in the system not rigidly bound to other particles we would have three further co-ordinates in a frame of reference having this point as origin. If any rigid bodies entered into the constitution of the system, each of these would introduce six co-ordinates. These co-ordinates (in most practical applications they are Cartesian or polar co-ordinates, with Eulerian angles in the case of rigid bodies) are denoted usually by symbols such as q_1, q_2, \dots, q_β , where β is the number just necessary and sufficient for complete description of the configuration of the system. The Cartesian co-ordinates of every particle or element of volume of the system can be expressed as functions of q_1, q_2, \dots, q_β ; *e.g.*,

$$\begin{aligned} x_r &= \phi_r(q_1, q_2, \dots, q_\beta) \\ y_r &= \psi_r(q_1, q_2, \dots, q_\beta) \\ z_r &= \chi_r(q_1, q_2, \dots, q_\beta). \end{aligned} \quad *$$

The velocity of each particle or element of volume is given by

$$\dot{x}_r = \frac{\partial \phi_r}{\partial q_1} \dot{q}_1 + \frac{\partial \phi_r}{\partial q_2} \dot{q}_2 + \dots + \frac{\partial \phi_r}{\partial q_\beta} \dot{q}_\beta,$$

and two similar equations.

Recalling the expression for kinetic energy, *viz.*, $\frac{1}{2} \Sigma m_r(\dot{x}_r^2 + \dot{y}_r^2 + \dot{z}_r^2)$, it is clear that the kinetic energy of

* In certain special cases t is also involved in the functional form, *i.e.*, the geometrical equations involve the time explicitly.

the system is given by a homogeneous quadratic function of the generalised components of velocity $\dot{q}_1, \dot{q}_2, \dots, \dot{q}_\beta$, the coefficients of the squared and product terms being in general, not constants, but functions of the co-ordinates. Denote this by

$$\frac{1}{2} (a_{11} \dot{q}_1^2 + \dots + a_{\beta\beta} \dot{q}_\beta^2 + 2 a_{12} \dot{q}_1 \dot{q}_2 + \dots) \quad (24.1.1)$$

The generalised components of momentum, denoted by p_1, p_2, \dots, p_β , are obtained by differentiating this expression with respect to $\dot{q}_1, \dot{q}_2, \dots, \dot{q}_\beta$, respectively. Thus

$$p_r = a_{r1} \dot{q}_1 + a_{r2} \dot{q}_2 + \dots + a_{r\beta} \dot{q}_\beta$$

where it is implied that $a_{rs} = a_{sr}$. It is now possible to express the kinetic energy in terms of the components of momentum. It is also a homogeneous quadratic function of these, such as

$$\frac{1}{2} (b_{11} p_1^2 + \dots + b_{\beta\beta} p_\beta^2 + 2 b_{12} p_1 p_2 + \dots) \quad (24.1.2)$$

where the coefficients b_{rs} are in general functions of the co-ordinates.

The potential energy of the system, whether arising from inter-action between its parts or from action between these and external bodies is a function of the co-ordinates $V(q_1, q_2, \dots, q_\beta)$, or briefly $V(q)$, involving among its parameters any quantities necessary for specifying the relations of the system to such external bodies. The sum of this function and the function expressed in (24.1.2) is called the "Hamiltonian function" of the system. Let us denote it by $E(q_1, q_2, \dots, q_\beta, p_1, p_2, \dots, p_\beta)$, or briefly $E(q, p)$; its value for given values of the q_r and p_r is, of course, equal to the energy of the system when in that phase of configuration and motion. The importance of this function lies in the fact that nearly a century ago the Irish mathematician, Sir William Rowan Hamilton, demonstrated that the equations of motion of the system could be written in the form

$$\begin{aligned} \frac{dq_r}{dt} &= \frac{\partial E(q, p)}{\partial p_r} \\ \frac{dp_r}{dt} &= -\frac{\partial E(q, p)}{\partial q_r} \end{aligned} \quad \dots \quad (24.1.3)$$

there being β equations of the first type, and β of the second. Even in the case of non-conservative systems where the forces cannot all be derived from a potential function, provided such forces are functions of the co-ordinates, we can write the equations of motion

$$\begin{aligned}\frac{dq_r}{dt} &= \frac{\partial E(q, p)}{\partial p_r} \\ \frac{dp_r}{dt} &= -\frac{\partial E(q, p)}{\partial q_r} + Q_r(q)\end{aligned}\quad . \quad (24.1.4)$$

where the β functions $Q_r(q)$ of the *co-ordinates* depend on the forces which are not included in the potential function $V(q)$. Representing dq_r/dt , or \dot{q}_r , and dp_r/dt , or \dot{p}_r , by u_r and v_r respectively, we see that each of the u_r and v_r are functions of the phase quantities $q_1, q_2, \dots, q_\beta, p_1, p_2, \dots, p_\beta$. Further, it follows from (24.1.3) or (24.1.4) that

$$\begin{aligned}\frac{\partial u_r}{\partial q_r} &= \frac{\partial^2 E(q, p)}{\partial q_r \partial p_r} \\ \frac{\partial v_r}{\partial p_r} &= -\frac{\partial^2 E(p, q)}{\partial p_r \partial q_r}\end{aligned}$$

Hence we obtain

$$\sum_{r=1}^{\beta} \left(\frac{\partial u_r}{\partial q_r} + \frac{\partial v_r}{\partial p_r} \right) = 0 \quad . \quad . \quad (24.1.5).$$

24.2 Liouville's Theorem.—We can now prove the general theorem mentioned in the last chapter for an ensemble of systems all identical in nature but of any degree of complexity. Each system of the ensemble has its own individual history, but the initial conditions of each system have been so chosen that at time t , the phase of any system is different to that of any other. Yet the number of systems in the ensemble is so great that within a finite extension-in-phase there are an enormous number of them. An element of this extension-in-phase can be specified by the limiting values

$$\begin{aligned}q_1 - \frac{1}{2} \delta q_1, \dots, q_\beta - \frac{1}{2} \delta q_\beta, p_1 - \frac{1}{2} \delta p_1, \dots, p_\beta - \frac{1}{2} \delta p_\beta \text{ and} \\ q_1 + \frac{1}{2} \delta q_1, \dots, q_\beta + \frac{1}{2} \delta q_\beta, p_1 + \frac{1}{2} \delta p_1, \dots, p_\beta + \frac{1}{2} \delta p_\beta,\end{aligned}$$

meaning that a phase in this extension is given by $q_1 \pm a_1, \dots, q_\beta \pm a_\beta, p_1 \pm b_1, \dots, p_\beta \pm b_\beta$ where a_1, \dots, b_β are 2β small positive quantities less in numerical value than $\frac{1}{2} \delta q_1, \dots, \frac{1}{2} \delta p_\beta$ respectively. The number of systems of the ensemble within this element at time t is

$$\rho \delta q_1 \dots \delta q_\beta \delta p_1 \dots \delta p_\beta$$

where ρ is a function of the q_r and p_r and t , say $f(q, p, t)$. To find the number at time $t + \delta t$ we must calculate the net gain of systems within these limits in time δt , due to the fact that the phase of each system has altered in the interval. If δt is chosen small enough, systems which have at time t phases given by

$$q_1 - \frac{1}{2} \delta q_1 - h_1, q_2 \pm a_2, \dots, q_\beta \pm a_\beta, p_1 \pm b_1, \dots, p_\beta \pm b_\beta,$$

and which are therefore outside the element at time t will be within the element at time $t + \delta t$, provided h_1 is not greater than $(u_1 - \frac{1}{2} \partial u_1 / \partial q_1 \cdot \delta q_1) \delta t$. On the other hand those whose phases at time t are given by

$$q_1 + \frac{1}{2} \delta q_1 - k_1, q_2 \pm a_2, \dots, q_\beta \pm a_\beta, p_1 \pm b_1, \dots, p_\beta \pm b_\beta,$$

and which are within the element at time t will be outside it at time $t + \delta t$ provided k_1 is not greater than $(u_1 + \partial u_1 / \partial q_1 \cdot \delta q_1) \delta t$. The net loss of systems to this element in the interval δt on this account will be given by

$$\frac{\partial(\rho u_1)}{\partial q_1} \delta q_1 \delta t \delta q_2 \dots \delta q_\beta \delta p_1 \dots \delta p_\beta.$$

Proceeding in this way the complete net loss in the interval δt is given by

$$\delta t \delta q_1 \dots \delta q_\beta \delta p_1 \dots \delta p_\beta \times \left\{ \frac{\partial(\rho u_1)}{\partial q_1} + \dots + \frac{\partial(\rho u_\beta)}{\partial q_\beta} + \frac{\partial(\rho v_1)}{\partial p_1} + \dots + \frac{\partial(\rho v_\beta)}{\partial p_\beta} \right\}$$

But the net gain is also

$$\frac{\partial \rho}{\partial t} \delta t \delta q_1 \dots \delta q_\beta \delta p_1 \dots \delta p_\beta.$$

Hence, since these expressions must be consistent we have the fundamental result

$$\frac{\partial \rho}{\partial t} + \frac{\partial (\rho u_1)}{\partial q_1} + \dots + \frac{\partial (\rho v_\beta)}{\partial p_\beta} = 0 \quad (24.2.1)$$

But by reason of (24.1.5) this reduces to

$$\frac{\partial \rho}{\partial t} + \Sigma u_r \frac{\partial \rho}{\partial q_r} + \Sigma v_r \frac{\partial \rho}{\partial p_r} = 0 \quad (24.2.2)$$

Now the system of the ensemble which was at the phase q_1, \dots, p_β at the time t is at the phase $q_1 + u_1 \delta t, \dots, p_\beta + v_\beta \delta t$ at time $t + \delta t$ and the density-in-phase of the ensemble at this phase is $f(q + u\delta t, p + v\delta t, t + \delta t)$ or

$$\rho + \Sigma u_r \frac{\partial \rho}{\partial q_r} + \Sigma v_r \frac{\partial \rho}{\partial p_r} + \frac{\partial \rho}{\partial t},$$

which, on account of the condition (24.2.2), is just ρ . This establishes the general theorem referred to in the previous chapter. Expressed in other words this means that if a particular system of the ensemble is at a phase q_1, \dots, p_β at time t and ρ is the limit of the number of systems within an element of extension-in-phase $q_1 \pm a_1, \dots, p_\beta \pm b_\beta$ at that time divided by $2^\beta a_1 \dots a_\beta 2^\beta b_1 \dots b_\beta$ when a_1, \dots, b_β are indefinitely reduced, and if the particular system is at phase q'_1, \dots, p'_β at time t' and ρ' is a like limit at time t' , then $\rho = \rho'$. The use of the methods of the calculus imply that we must conceive the number of systems in a finite extension-in-phase to be increased without limit, just as in hydrodynamics we conceive a fluid to be a continuous medium. There is still another way of looking at this important proposition. We can assume that all the phases in a certain finite extension-in-phase satisfy the condition that each of them make a function $\phi(q, p)$ of q_1, \dots, p_β negative or zero in value. Using geometrical language we can say that those phases which make the function zero are on the "hypersurface," $\phi(q, p) = 0$, and the others "within" it. Suppose a number of systems of the ensemble are at these phases at time t . At time t' they are at other phases, and from the dynamical equations q'_1, \dots, p'_β can be expressed as functions of q_β, \dots

p_β and $t' - t$, so that we can obtain a function $\psi(q', p')$ of q'_1, \dots, p'_β which is equal to $\phi(q, p)$. Then all the systems at time t' will be within the hypersurface

$$\psi(q, p) = 0,$$

or on it. Liouville's theorem then states that the integration of $dq_1 \dots dq_\beta dp_1 \dots dp_\beta$ throughout the extension determined by $\phi(q, p)$ being zero or negative yields an integral equal in value to that obtained by integrating $dq_1 \dots dq_\beta dp_1 \dots dp_\beta$ throughout the extension determined by $\psi(q, p)$ being zero or negative. Thus there is a conservation of the extension-in-phase occupied by a group of systems distributed continuously in a finite extension to begin with.

One word of caution is necessary. The actual systems which lie within the "rectangular" element $q_1 \pm a_1, \dots, p_\beta \pm b_\beta$ at time t , are not in general the same as those which lie within the rectangular element $q'_1 \pm a_1, \dots, p'_\beta \pm b_\beta$ at time t' . The number is the same, but identity is not necessarily preserved. Put in geometrical language, the "shape" of $\phi(q, p) = 0$ is not necessarily the same as that of $\psi(q, p) = 0$. If a rigid body moves in our perceptual space, certain relations must hold between the co-ordinates x, y, z of a particle of it at time t , and the co-ordinates x', y', z' of the same particle at time t' by reason of the fact that the moving thing is rigid and preserves its shape. But no analogous relations hold between q_1, \dots, p_β and q'_1, \dots, p'_β ; at all events Liouville's theorem makes no such claim; it simply proves conservation of the extension.

Last of all we have clearly *not* proved that $\partial\rho/\partial t$ is zero, or that the density-in-phase about a particular phase is conserved.

It is, of course, understood in all this that no system of an ensemble acts on any other system; each pursues its predestined dynamical "path," under the influence of its own internal interactions or of the actions of external bodies, and it should be carefully noted that the disposition of external bodies is supposed to be alike for each system.

Each member of the ensemble is really system plus external bodies. At a given instant the phase-quantities which determine the configuration and motion of the various parts of a system differ from the member to member of the ensemble, but those parameters which determine configuration and motion of the external bodies are alike for all members. These parameters may, of course, change in time, but at a given instant they have identical values for all the members. As an example of this we have the ensemble of rain-drops or pendula treated in the last chapter. Another example, an ensemble of gas systems, is treated on the assumption that each one is enclosed in one of an enormous group of identical vessels, *i.e.*, each one is subject to an external field of force which is alike for all.

24.3 Microscopic States and Their Probabilities.—A “microscopic state” of a system is defined by stating that the phase of the system lies within a small rectangular element of extension-in-phase about a particular central phase.

Now the successive phases of an actual system must, by the laws of dynamics, satisfy the relation

$$E(q, p) = \text{constant.}$$

These are, in fact, in geometrical language, the energy hypersurfaces, and the dynamical path lies on one of them. It is clear, therefore, that the phases possible to a system with a given energy do not occupy an extension with the full dimensionality, 2β , of the ensemble. We can, however, conceive an ensemble of systems limited in such a way that no system has an energy less than a definite value X , and none has a value more than a value $X + \delta X$, greater by an infinitesimal amount. Imagine also that at any instant the systems of the ensemble are so distributed in phase that their density-in-phase is uniform throughout the extension bounded by the hypersurfaces.

$$E(q, p) = X$$

$$E(q, p) = X + \delta X \quad . \quad . \quad . \quad (24.3.1).$$

Liouville's theorem then shows that this state of things is

perpetual. In fact, since at time t , the $\partial\rho/\partial q$, and $\partial\rho/\partial p$, are all zero, it follows that

$$\frac{\partial\rho}{\partial t} = 0$$

also. Thus the ensemble is in statistical equilibrium. There is no tendency for the systems to crowd into any particular part of the extension defined by (24.3.1) at the expense of other parts.

Imagine that we are endowed with the power of making a choice of one system out of the ensemble. We are just situated in a position similar to a person asked to select any ball out of a number of boxes each containing the same number of balls. The chance that the choice will fall within a certain box is $1/A$ if there are A boxes. So the chance that we select a system within a given microscopic state is $1/A$ if the extension defined by (24.3.1) is divided into A equal elementary extensions. Or to put it another way, all the different microscopic states of the ensemble have equal probabilities. Further, this chance is not upset with lapse of time, as would have been the case had Liouville's theorem not been true, for then systems would have crowded in increased numbers into certain regions of the complete extension, giving, therefore, after a time, an enhanced probability that one of the microscopic states within this region would contain the system chosen, the chances elsewhere being on the other hand diminished.

An actuary, it is well known, when preparing tables for insurance or other purposes does not base his calculations on the facts concerning one or two individuals, but on averages extending over large groups representative of each section of a community of individuals. Our point of view at this stage is very like that of the actuary. We really have not been basing our statistical calculations in the preceding chapters on the behaviour of a single molecular system, but on the average behaviour of a large representative group of systems, members of an ensemble. Each system is composed of the same number n of molecules, all of the same kind, each with f degrees of freedom. If more

than one type is present, each system contains n molecules of one type each with f degrees of freedom, n' of a second type each with f' degrees, and so on. The number of degrees of freedom of the system is nf , or $nf + n'f' +$, etc., as the case may be. Thus in the case of one type of molecule if $q_{11}, q_{12} \dots, q_{1f}$ denote the co-ordinates of the first molecule in the system $q_{21}, q_{22}, \dots, q_{2f}$ those of the second molecule, and so on, then the co-ordinates of the *system* are q_{11}, \dots, q_{nf} , the number being nf in all; in short, the suffix β of the preceding portion of this chapter is nf (or $nf + n'f' +$ etc.). It is very necessary to be on guard here against a fatal misconception. In a sense a molecular system is an ensemble, for it contains an enormous number of molecules, and each molecule is in itself a dynamical system. But that is not the sense in which the word ensemble is used here. For one thing, the molecules interact on one another, and Liouville's theorem certainly does not hold for a molecular system regarded as an ensemble of molecules. The systems must be regarded as independent of each other, each pursuing its own dynamical path uninterfered with by any other system if Liouville's theorem is to be true. It is as well to introduce here a simple notation to indicate the distinction made. We have in the past spoken of representing the momenta and co-ordinates of a molecule in a phase-diagram or "phase-space" with dimensions $2f$; we shall refer to this as the M-space. But now we must also think of a phase-space in which a whole molecular system is represented by a *single* "point." Such a space has a dimensionality 2β , where $\beta = nf$ (or $nf + n'f' +$ etc.). We shall call this the G-space. (Gibbs' phase-space.) It is in this space that an ensemble of systems is represented by a "cloud of points."

A microscopic state of the system is obtained by assigning narrow limits to the β co-ordinates and β momenta of the system. A moment's thought will show that this is tantamount to assigning a complexion to the molecules of a molecular system. Thus if all the systems are considered to have values of energy practically the same for each, *i.e.*, between narrow limits such as X and $X + \delta X$, then each

complexion of the system, which is indicated by assigning n_1 particular molecules to the first phase-cell in the M-space, n_2 to the second, . . . , n_c to the c^{th} , has, as it were, one particular phase-cell in the G-space within the shell between the two hypersurfaces as its home. A statistical state of the system is therefore associated with a particular group of phase-cells in the G-space, the number in the group being $n!/(n_1! n_2! \dots n_c!)$. But we have seen that all but a relatively insignificant number of complexions are embraced within a statistical state in which the number of molecules in an M-phase-cell, corresponding to molecular energy ϵ , is proportional to $e^{-\mu\epsilon}$ (where $3/2\mu$ is the average kinetic energy of translation of a molecule) or agrees very closely to this distribution. This means that if we fill the shell in the G-space with a uniformly dense cloud of representative points, then on choosing one at random there is an enormous probability that we shall select one which represents a system in, or very near to the Maxwell-Boltzmann distribution of molecular co-ordinates and momenta. Moreover, and this is where Liouville's theorem comes in, this state of affairs if arranged for initially is not upset in course of time. The distribution in the G-space remains uniform, and so on, returning to make a choice at a later instant the chances are still enormously in favour of selecting a representative point associated with a system in or near the Maxwell-Boltzmann distribution. In other words, this distribution is a normal property of the system. The word "normal" was suggested by Jeans as a convenient epithet for any property which is common or nearly common to every member of the ensemble distributed in a uniform manner throughout a region of the G-space. As giving point to the warning uttered above, the reader will observe that the distribution of representative points in a uniform manner in the G-space does not lead to uniform distribution of M-representative points in the M-space, except in relatively few cases. An enormous preponderance lies with a very non-uniform distribution in the latter space.

This is essentially an actuarial process, and actuaries know that, for the purposes involved, although the life of a

given individual may in its course be seriously at variance with the average life of the whole community, yet things will work out alright in the end on the assumption that it is the same in certain particulars. This is essentially the hypothesis we introduce at this point of our reasoning. Dynamics can carry us no further. It has had its say. A given molecular system *might* behave very differently from one which is always in or near the Maxwell-Boltzmann distribution. There do exist relatively very small regions of extension-in-phase in the G-space where matters are very different for any system whose representative point happens to be there, and we cannot definitely deny the statement that once there it will always remain in such a region, or that the greater part of its path may lie in such regions. All we can say is that it is unlikely. But the reader must carefully note that in carrying over what is undoubtedly a proven statement for the average behaviour of all the systems in an ensemble at any instant, for application to a single system, and asserting that such is the average behaviour of a single system *throughout a long time*, we are taking a step which is undoubtedly plausible, but which cannot be definitely proved. The hypothesis was called by Maxwell the "principle of continuity of path" and by Boltzmann the "ergodic hypothesis." It amounts to an assumption that a given molecular system will in course of time pass through all the complexions consistent with its energy, or at all events through a large group of them sufficiently representative to them all, before returning to or very near to some original phase, and thereafter pursuing the same path as before. Yet it must be admitted that the dynamical systems which have been most thoroughly worked out in detail by the mathematicians, *viz.*, the astronomical systems, give little or no support to this view. Indeed we can realise that our own solar system, if absolutely free from all external influence and left to the internal gravitational action of its parts, would go on cycle after cycle, much as it is, never approaching in successive ages unlimited phases which we can conceive it to have by tumbling planets and orbits about in our imagination. There is,

of course, an intuitive feeling that the very complexity of molecular systems and the multiplicity of their parts favour the hypothesis, but this feeling does not constitute proof. Perhaps the most helpful idea is contained in the undoubted facts that any molecular system can hardly, in practice, be said to be free from other influences than those ostensibly introduced in theoretical discussion. For example, even in a thermostat slight fluctuations of energy must go on in any system; this means that though for a time the system may pursue a definite path on one energy hypersurface, presently it will be "displaced" to another on a neighbouring hypersurface; and although any one path might be far from traversing a sufficiently representative group of microscopic states, yet the fortuitous shifting from path to path may produce this result in the long run, and effectively prevent any system from remaining in a freak region of extension-in-phase for anything but a negligible period.

The "freak" regions are relatively very small, and any system might be compared to a man blindfolded and left to wander at random in a large field. The chance that he would walk into a small circle drawn in a particular spot on this field is small. If in the circle, the chance that he would remain in it and not wander out of it is also small. There is no impossibility in his walking into the circle and "depressing his entropy," but in all likelihood his entropy will soon rise again, and he will walk out of it.

Let the reader also recall the example given in the previous chapter, where an ensemble of simple systems, compactly grouped in the beginning, "spread themselves out" without contradicting the law of density-conservation; so that a choice at the beginning would have given one of a rather restricted group of phases, while at a later time a choice would be made from a group of phases more representative of all the phases possible. The reader should in this connection consult Gibbs' *Elementary Principles*, Chapter XII.

The ensemble method is very powerful in dealing directly with problems where we are concerned with a system which

is not isolated, and it is a question of the probability that it contains a certain energy, or rather that its energy is within certain narrow limits. This probability is proportional to the number of microscopic states consistent with these energy limits, *i.e.*, to the magnitude of the extension-in-phase bounded by the energy-hypersurfaces corresponding to the upper and lower limits. Of course, when quantum assumptions come in we have to modify this strictly classical result in a manner which will be obvious on glancing back at Chapter XVI. A microscopic state surrounding a particular phase is the element in the classical discussion; in the quantum discussion the element is the whole succession of phases in a given quantum state. The probability in the one case is the magnitude of the G-phase-cell of dimensionality 2β , *i.e.*, having physical dimensions equal to action raised to the power β . In the other it is h^β . To illustrate this procedure we shall return to a fresh discussion of the entropy-constant problem, but before doing so we must point out the importance of choosing momentum instead of velocity to indicate phase. We have indulged in this practice throughout, and the cause is clear. The elegant form of Hamilton's equations, leading as they do to the fundamental statistical theorem on density-conservation, depend entirely on choosing the p_r , and not the \dot{q}_r , as indicating the motion aspect of the phase. In a phase-diagram in which q_r and \dot{q}_r are represented there is no conservation of density of representative points around a moving phase, and no simple basis for probability calculation presents itself.

24.4 The Entropy-Constant Once More.—Let us consider once more a system of n simple monatomic molecules represented by a point in a G-space of $6n$ dimensions. Suppose the system to be in a state in which a *particular* atoms are in the gaseous state, and the remaining b *particular* atoms are in a solid cubic lattice, and arranged in a *particular way* in the lattice.

To simplify the discussion we will also assume that the lattice is also in its lowest quantum state, so that its energy is $b\epsilon$ where ϵ is a constant. In order that any molecule

may leave the lattice and enter the gaseous state its potential energy must be increased by an amount w . Hence, if K is the kinetic energy of the gaseous molecules, then $K + aw + b\epsilon$ must lie between χ and $\chi + \delta\chi$. Regarding for a moment the gas molecules as a separate system with $3a$ degrees of freedom, the probability that it will contain an amount of energy whose value lies between $\chi - aw - b\epsilon$ and $\chi - aw - b\epsilon + \delta\chi$ is proportional to the magnitude of the extension in a $6a$ -dimensional phase-space bounded by the energy hypersurfaces

$$(\xi_1^2 + \eta_1^2 + \zeta_1^2 + \dots + \xi_a^2 + \eta_a^2 + \zeta_a^2) \\ = 2m(\chi - aw - b\epsilon),$$

and

$$(\xi_1^2 + \eta_1^2 + \zeta_1^2 + \dots + \xi_a^2 + \eta_a^2 + \zeta_a^2) \\ = 2m(\chi - aw - b\epsilon + \delta\chi).$$

It will be shown in a note at the end of the chapter that this is

$$\frac{(2\pi m)^c}{(c-1)!} v^a (\chi - aw - b\epsilon)^{c-1} \delta\chi \quad (24.4.1)$$

where v is the volume of the gas, *practically* of the containing vessel, and $c = 3a/2$, a being assumed to be an even number.

Since we have limited the lattice to one quantum state, *viz.*, the lowest consistent with the number of molecules in it, the probability that it is in this state is given by an extension in a $6b$ dimensional phase-space. This is h^{3b} according to the quantum postulate just referred to. Thus the probability that the a particular molecules are in the gas and the remaining b in the lattice arranged in a particular way and in their lowest quantum state is given by an extension in a $6n$ -dimensional phase-diagram, whose magnitude is

$$\frac{h^{3b} v^a (2\pi m)^c (\chi - aw - b\epsilon)^{c-1}}{(c-1)!} \delta\chi \quad (24.4.2).$$

The probability that *any* a molecules may be in the gaseous state, and the remaining b , still arranged in one way in the lowest quantum state, in the solid is obtained by multiplying (24.4.2) by $n!/(a!b!)$, which is the number of

ways of choosing a molecules out of n . But this has still to be multiplied by $b!$ to introduce all those complexions which correspond to *any* arrangement of the b molecules in the lattice. Thus the probability that there are a molecules in the gaseous state out of the total number n , is

$$\frac{n!}{a!(c-1)!} h^{3b} v^a (2\pi m)^c (\chi - aw - b\epsilon)^{c-1} \delta\chi \quad (24.4.3).$$

The most probable value of a is found by finding a maximum value of this expression, subject to the condition that χ and $\delta\chi$ are constant. Referring to the expression (24.4.3), with $n!$ and $\delta\chi$ omitted, as P, we, as usual, take logarithms and use Stirling's theorem. Thus,

$$\begin{aligned} \log P = & 3(n-a) \log h + a \log v + \frac{3a}{2} \log (2\pi m) \\ & + \frac{3a}{2} \log [\chi - n\epsilon + a(\epsilon - w)] - \frac{5a}{2} \log a + \frac{5a}{2} - \frac{3a}{2} \log \frac{3}{2}.^* \end{aligned}$$

If we now write down the condition that $d \log P/da$ is zero we find, after a little re-arrangement, that a is determined by the equation

$$\begin{aligned} \frac{5}{2} \log a - \frac{3}{2} \log [\chi - n\epsilon + a(\epsilon - w)] - \frac{3a}{2} \frac{\epsilon - w}{\chi - n\epsilon + a(\epsilon - w)} \\ = -3 \log h + \log v + \frac{3}{2} \log 2\pi m - \frac{3}{2} \log \frac{3}{2}. \end{aligned}$$

If we now connect this statistically most probable distribution with the macroscopic experimental state, for which the given total energy χ determines, with the volume v and the number a , the temperature θ , we know that $\chi - aw - b\epsilon$, being the kinetic energy of the gaseous molecules, is $(3/2) a k \theta$; further we know that the pressure p of the gas is $a k \theta/v$, since v is practically the volume of the gas. Hence, since $\log p = \log a - \log v + \log k\theta$ we readily find that

$$\begin{aligned} \log a - \frac{3}{2} \log k\theta - \frac{\epsilon - w}{k\theta} \\ = -3 \log h + \log v + \frac{3}{2} \log (2\pi m) \end{aligned}$$

* In practice a is so large that we can replace $3a/2 - 1$ by $3a/2$.

$$\begin{aligned}\text{or } \log p &= -\frac{w}{k\theta} + \frac{\epsilon}{k\theta} + \frac{5}{2} \log(k\theta) + \frac{3}{2} \log(2\pi m) - 3 \log h \\ &= -\frac{w}{k\theta} + \frac{\epsilon}{k\theta} + \frac{5}{2} \log \theta + \log \frac{(2\pi m k)^{\frac{3}{2}} k}{h^3}.\end{aligned}$$

This is the vapour-pressure equation for the simple model we have chosen. It clearly corresponds to the general thermodynamic equation (21.2.8) in Chapter XXI.

$$\begin{array}{lll}-\frac{w}{k\theta} & \text{corresponds to} & -\frac{L_o}{R\theta} \\ \frac{\epsilon}{k\theta} & \text{,,} & \text{,,} -\frac{1}{R} \int_0^\theta \frac{E(x)}{x^2} dx \\ \frac{5}{2} & \text{,,} & \text{,,} \frac{s_p}{R} \\ \gamma & \text{,,} & \text{,,} \log \frac{(2\pi m k)^{\frac{3}{2}} k}{h^3}.\end{array}$$

The method which is due to Ehrenfest and Trkal is somewhat less laborious than Stern's, and differs from his most signally in the fact that it treats the statistical considerations on a quantum basis, while Stern's treats the statistics on classical lines, while applying quantum methods to the thermodynamical investigation.

24.5 Gibbs' Canonical Ensemble.—In order that an ensemble may form the actual basis for a statistical treatment of a dynamical system, it is necessary that the ensemble should be in statistical equilibrium. This means that the density-in-phase of the ensemble round a *given phase* must not change in time, *i.e.*, that $\partial\rho/\partial t$ must be zero. Now this condition is not generally true. Liouville's theorem demonstrates that the density around a dynamically-moving phase, *i.e.*, around the "point" representative of a *given system*, is constant, *i.e.*, that $\partial\rho/\partial t + \sum \dot{q}_r \partial\rho/\partial q_r + \sum \dot{p}_r \partial\rho/\partial p_r$ is zero. It is therefore necessary for the statistical equilibrium of the ensemble that the condition

$$\sum_{r=1}^f \left(\dot{q}_r \frac{\partial\rho}{\partial q_r} + \dot{p}_r \frac{\partial\rho}{\partial p_r} \right) = 0 \quad . \quad . \quad (24.5.1)$$

be satisfied. If this is so, any assumption that the probability of a given microscopic state being occupied by a single system at a chosen instant is proportional to the density of ensemble at the central phase of that microscopic state, will not be upset with lapse of time, as would be the case if the conditions of density around given phases kept altering.

The simplest type of ensemble satisfying (24.5.1) is, as we have seen, one uniformly distributed in phase, but it is by no means the only one. If, for instance, the density is chosen initially at each phase to be a function of the energy associated with that phase, (24.5.1) is satisfied in cases where the energy of the system is conserved ; for if

$$\rho = f(\chi)$$

where χ is the value at the phase of the Hamiltonian function $E(q, p)$ of the system ; then

$$\frac{\partial \rho}{\partial q_r} = \frac{df(\chi)}{d\chi} \cdot \frac{\partial E(q, p)}{\partial q_r}$$

and

$$\frac{\partial \rho}{\partial p_r} = \frac{df(\chi)}{d\chi} \cdot \frac{\partial E(q, p)}{\partial p_r}$$

and so

$$\begin{aligned} \sum_{r=1}^{\beta} \left(\dot{q}_r \frac{\partial \rho}{\partial q_r} + \dot{p}_r \frac{\partial \rho}{\partial p_r} \right) &= \frac{df(\chi)}{d\chi} \left(\frac{dq_r}{dt} \frac{\partial E(q, p)}{\partial q_r} + \frac{dp_r}{dt} \frac{\partial E(q, p)}{\partial p_r} \right) \\ &= \frac{df(\chi)}{d\chi} \cdot \frac{dE(q, p)}{dt} \\ &= 0.* \end{aligned}$$

If we wish to maintain other suitable mathematical conditions for the ensemble as well as that of statistical equilibrium, the function $f(\chi)$ must be subject to other conditions. Thus $f(\chi)$ should not be infinite anywhere. The reader may think this condition strange in view of the fact that we have several times postulated an increase of the number of systems in the ensemble to an enormous value so as

* Note that this result is only true for conservation of energy. In other cases the right-hand side is $\sum Q_r \dot{q}_r$. See Hamilton's equations.

to produce conditions approximating to a "continuous fluid" of representative points in the G-phase-space. But this is not really the same thing. The function $f(\chi)$ must not become merely an indeterminate infinity anywhere as it would do if it were put equal to, say χ^{-1} or $\tan \chi$, or so forth. Writing it as $N \phi(\chi)$, where there are N systems in the ensemble, we see that

$$\int \phi(\chi) dq_1 \dots dp_\beta$$

over the whole phase-diagram must be unity, and this clearly debars us from the choice of many functions. Thus $\phi(\chi)$ cannot be simply proportional to χ , nor can it have the same constant value everywhere, although we may give it a suitable constant value between a pair of energy hypersurfaces and make it zero elsewhere, as, indeed, we did in the preceding considerations.

Gibbs points out that an ensemble distributed in such a way that the density-in-phase is at all phases proportional to

$$\exp \left[- \frac{E(q, p)}{\Theta} \right] \quad . \quad . \quad . \quad (24.5.2)$$

where Θ is a constant, which he calls the "modulus of distribution," "seems to represent the most simple case conceivable, since it has the property that when the system consists of parts with separate energies, the laws of distribution-in-phase of the separate parts are of the same nature—a property which enormously simplifies the discussion, and is the foundation of extremely important relations to thermodynamics." Such an ensemble he names "canonical." An ensemble with a constant density between two very near energy-hypersurfaces, and a density which is zero elsewhere, he calls "microcanonical."

A considerable part of Gibbs' "Elementary Principles" is devoted to working out the properties of canonical ensembles and showing how the rational foundation of thermodynamics is related to them. There is no need to go into the matter very fully here. Gibbs' work is certainly not easy reading for a beginner; but the reader who has

struggled through the previous pages to this point is no longer a beginner. The author feels that he can be safely left at this point to pursue his further studies in this classic of Statistical-Mechanical theory, and will bring this book to a close with a few remarks on the canonical ensemble.

In the first place one must carefully guard against confusing the Maxwell-Boltzmann law of distribution of molecular co-ordinates and momenta in a system of molecules with Gibbs' specification of a canonical ensemble of dynamical systems. On the assumption that the probability of a statistical state of a molecular system is proportional to the number of complexions consistent with it one can deduce the result that the number of molecules in a given element of phase-extension (*i.e.*, M-phase) is proportional to $e^{-\epsilon/kT}$ where ϵ is the energy of a molecule at the central phase *in the most probable state*. But this statement implies no necessity that this is true all the time. There are undoubtedly fluctuations from this state, such fluctuations being less marked the greater the number of molecules in the system. Gibbs on the other hand considers ensembles of systems. These systems are not necessarily molecules nor even groups of molecules, although his work finds its most ready application in dealing with systems of molecules. His system is any group of objects subject to dynamical law. Further, the systems of the ensemble are isolated from one another. Whatever law of distribution is laid down for them, they follow Liouville's law, and under certain conditions this implies statistical equilibrium with no fluctuation. The $\exp(-E/kT)$ law satisfies these conditions, and is *laid down* by Gibbs on grounds of mathematical convenience, and because of its ready application to practical problems, qualifications which are illustrated freely in his book. Of course, if we choose to regard the individual systems as huge molecules and imagine them to be all immersed in an enormous body of gaseous fluid (a "temperature-bath"), we could appeal to the Maxwell-Boltzmann result and prove that the systems would, except on rare occasions, be distributed in phase, as Gibbs laid down for his canonical ensemble; and this explains why in

recent literature, references to Gibbs' canonical ensemble as a "temperature-bath" occasionally occur. Indeed, in Chapters XX. to XXIII., this point of view has been actually adopted at certain parts of the argument.

Of course, the expression $\exp(-E/\Theta)$ is multiplied by a constant factor in the specification of a canonical system, and Gibbs writes his rule in the form

$$N \exp \left[\frac{\Psi - E(q, p)}{\Theta} \right] dq_1 \dots dp_\beta \quad (24.5.2)$$

where Ψ is a constant for every system, just as Θ is. In fact, Ψ is a function of Θ and the parameters of a system, the parameters, as already stated, being any quantities necessary to express unchanging metrical properties of a system or its dynamical relations to external bodies which, one must remember, are the same for all the systems at one moment. Ψ is determined in terms of Θ and the parameters a_1, \dots, a_e by the equation

$$\int \dots \int_{\text{all phases.}} \exp \left[\frac{\Psi - E(q, p)}{\Theta} \right] dq_1 \dots dp = 1$$

or

$$e^{-\frac{\Psi}{\Theta}} = \int \dots \int_{\text{all phases.}} e^{-\frac{E}{\Theta}} dq_1 \dots dp_\beta \quad (24.5.3).$$

Gibbs devotes several pages to the discussion of average values in a canonical ensemble. Thus if u is a function of co-ordinates, momenta and parameters, its average value over the whole ensemble is given by the expression

$$\int \dots \int_{\text{all phases.}} u \exp \left(\frac{\Psi - E}{\Theta} \right) dq_1 \dots dp_\beta \quad (24.5.4).$$

As an illustration let us work out the average value of $p_r \frac{\partial E}{\partial p_r}$ where p_r is any momentum. It is

$$\int \dots \int_{\text{all phases.}} p_r \frac{\partial E}{\partial p_r} \exp \left(\frac{\Psi - E}{\Theta} \right) dq_1 \dots dp_\beta.$$

Now by (24.5.3) this is equal to

$$\frac{\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} p_r \frac{\partial E}{\partial p_r} \exp\left(\frac{\Psi - E}{\Theta}\right) dp_1 \dots dp_\beta}{\int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \exp\left(\frac{\Psi - E}{\Theta}\right) dp_1 \dots dp_\beta} \quad (24.5.5).$$

But by integration by parts

$$\int_{-\infty}^{\infty} p \exp\left(\frac{\Psi - E}{\Theta}\right) \frac{\partial E}{\partial p_r} dp_r = \Theta \int_{-\infty}^{\infty} \exp\left(\frac{\Psi - E}{\Theta}\right) dp_r.$$

Hence (24.5.5) becomes simply Θ . Thus the average value of $p_r \partial E / \partial p_r$ for any momentum is the same for all.

Now $E = E_p + E_q$ where E_p is the kinetic energy and E_q is the potential. E_q is independent of the momenta, and E_p is a homogeneous quadratic function of the momenta. So

$$\begin{aligned} E_p &= \frac{1}{2} \sum_{r=1}^{\beta} p_r \frac{\partial E}{\partial p_r} \\ &= \frac{1}{2} \sum_{r=1}^{\beta} p_r \frac{\partial E}{\partial p_r} \\ &= \frac{1}{2} \beta \Theta. \end{aligned}$$

This is Gibbs' version of the equipartition of energy theorem. The kinetic energy of any system can be divided into β parts, and the average value of any part over the whole ensemble is the same, viz., $\frac{1}{2} \Theta$. Note that this theorem is not found for a time-average of a part for a single system, but for an average at one instant over all the systems of the ensemble.

Finally we shall show one of Gibbs' thermodynamic analogies. In equation (24.5.3) let us vary the modulus and parameters from the values Θ, a_1, \dots, a_e to $\Theta + \delta\Theta, a_1 + \delta a_1, \dots, a_e + \delta a_e$. We obtain

$$\begin{aligned} e^{-\frac{\Psi}{\Theta}} \left(\frac{\Psi}{\Theta^2} \delta\Theta - \frac{1}{\Theta} \delta\Psi \right) &= \delta\Theta \frac{1}{\Theta^2} \int_{\text{phases}}^{\text{all}} \int E e^{-\frac{E}{\Theta}} dq_1 \dots dp_\beta \\ &\quad - \frac{1}{\Theta} \sum_{s=1}^e \delta a_s \int_{\text{phases}}^{\text{all}} \int \frac{\partial E}{\partial a_s} e^{-\frac{E}{\Theta}} dq_1 \dots dp_\beta \end{aligned}$$

or

$$\begin{aligned} \frac{\Psi}{\Theta} \delta \Theta - \delta \Psi &= \delta \Theta \frac{1}{\Theta} \int_{\text{phases}}^{\text{all}} E \exp \left(\frac{\Psi - E}{\Theta} \right) dq_1 \dots dq_\beta \\ &\quad - \sum_{s=1}^e \delta a_s \int_{\text{phases}}^{\text{all}} \frac{\partial E}{\partial a_s} \exp \left(\frac{\Psi - E}{\Theta} \right) dq_1 \dots dq_\beta \end{aligned} \quad (24.5.6).$$

Now the expressions $-\partial E/\partial a_s$ represent the forces exerted by the system on the external bodies; for since E_p does not depend on the parameters which define the position of the external bodies, and since the energy entering the system through the action of external bodies is

$$\sum_{s=1}^e \frac{\partial E_q}{\partial a_s} \delta a_s$$

i.e.,

$$\sum_{s=1}^e \frac{\partial E}{\partial a_s} \delta a_s$$

it follows that the expressions $\partial E/\partial a_s$ represent the forces acting on the system due to external bodies. Writing \bar{A}_s for $-\partial E/\partial a_s$, i.e., the force exerted by the system on its environment through the parameter a_s , we can write (24.5.6) in the form

$$\delta \Psi = \frac{\Psi - \bar{E}}{\Theta} \delta \Theta - \sum_{s=1}^e \bar{A}_s \delta a_s \quad . \quad . \quad (24.5.7)$$

where we recall (24.5.4) and indicate an average value of quantity over the ensemble by drawing a bar over it.

Writing $\Phi(q, p, a)$ for the function $(\Psi - E)/\Theta$ and $\bar{\Phi}(a)$ for $(\Psi - \bar{E})/\Theta$ we have

$$\delta \Psi = \bar{\Phi} \delta \Theta - \sum_{s=1}^e \bar{A}_s \delta a_s$$

and since

$$\delta \Psi - \delta \bar{E} = \Theta \delta \bar{\Phi} + \bar{\Phi} \delta \Theta$$

it follows that

$$\delta \bar{\Phi} = - \frac{\sum_{s=1}^e \bar{A}_s \delta a_s}{\Theta} \quad . \quad . \quad (24.5.8).$$

The analogy with the entropy equation in thermodynamics is apparent. $\Phi(a)$ is the analogue of entropy, $\bar{E}(a)$ of the internal energy, $\Sigma \bar{A}_s \delta a_s$ of the work done by a thermodynamic system on its environment, Θ of the temperature, $\Psi(a)$ of the free energy.

NOTE ON THE INTEGRATION IN SECTION 24.4

If we integrate $d\xi_1 d\xi_2$ throughout a region of plane space defined by $\xi_1^2 + \xi_2^2 \leq r^2$ the result is πr^2 . We obtain from this result the integral of $d\xi_1 d\xi_2 d\xi_3$ throughout a region of space defined by $\xi_1^2 + \xi_2^2 + \xi_3^2 \leq r^2$ by means of the "zone" method. That is, we put it equal to

$$\begin{aligned} & 2 \int_0^r \pi (r^2 - x^2) dx \\ &= 2\pi r^3 - \frac{2\pi}{3} r^3 \\ &= \frac{4\pi r^3}{3}. \end{aligned}$$

If we now write $V_n(r)$ for the result of integrating $d\xi_1 d\xi_2 \dots d\xi_n$ throughout a range of values defined by

$$\xi_1^2 + \xi_2^2 + \dots + \xi_n^2 \leq r^2$$

we can obtain $V_n(r)$ from $V_{n-1}(r)$ in an analogous manner. Thus

$$\begin{aligned} V_n(r) &= 2 \int_0^r V_{n-1} \{(r^2 - x^2)^{\frac{1}{2}}\} dx \\ &= 2r \int_0^{\frac{\pi}{2}} V_{n-1}(r \cos \phi) \cos \phi d\phi \end{aligned}$$

where we write $r \sin \phi$ for x .

Putting $V_n(r) = A_n r^n$, where A_n is some numerical multiplier depending on n , we have

$$A_n = 2 A_{n-1} \int_0^{\frac{\pi}{2}} (\cos \phi)^n d\phi.$$

The definite integral is known to have the value

$$\frac{1 \cdot 3 \cdot 5 \cdot \dots \cdot (n-1)}{2 \cdot 4 \cdot 6 \cdot \dots \cdot n} \frac{\pi}{2} \text{ if } n \text{ is even,}$$

and $\frac{2 \cdot 4 \cdot 6 \dots (n-1)}{1 \cdot 3 \cdot 5 \dots n}$ if n is odd.

So

$$A_n = 2 \cdot \frac{1 \cdot 3 \cdot 5 \dots (n-1)}{2 \cdot 4 \cdot 6 \dots n} \frac{\pi}{2} A_{n-1} \text{ if } n \text{ is even}$$

and

$$A_n = 2 \cdot \frac{2 \cdot 4 \cdot 6 \dots n-1}{1 \cdot 3 \cdot 5 \dots n} A_{n-1} \text{ if } n \text{ is odd.}$$

$$\text{In either case } A_n = \frac{2\pi}{n} A_{n-2},$$

and thus since $A_2 = \pi$ and $A_3 = \frac{4\pi}{3}$, it is not hard to show that

$$V_n(r) = \frac{\pi^{\frac{n}{2}}}{\left(\frac{n}{2}\right)!} r^n \text{ if } n \text{ is even}$$

$$\text{and } = 2 \frac{(2\pi)^{\frac{n-1}{2}}}{1 \cdot 3 \cdot 5 \dots n} r^n \text{ if } n \text{ is odd.}$$

Taking n as even, the region within a "shell" bounded by

$$\xi_1^2 + \dots + \xi_n^2 = r^2$$

and

$$\xi_1^2 + \dots + \xi_n^2 = (r + \delta r)^2$$

is given by $\delta V_n(r)$, or

$$\frac{n}{2} \frac{\pi^{\frac{n}{2}}}{\left(\frac{n}{2}\right)!} (r^2)^{\frac{n}{2}-1} (\delta r^2)$$

which is equal to

$$\frac{\pi^{\frac{n}{2}}}{\left(\frac{n}{2} - 1\right)!} r^{n-2} 2r \delta r$$

In the text r^2 is $2m(E - aw - b\epsilon)$, and δr^2 or $2r \delta r$ is $2m \delta E$, while $n/2$ is $3a/2$ or c .

APPENDIX ON RECENT DEVELOPMENTS

QUITE recently, no later than 1924 in fact, an unexpected turn was given to the statistical theory of physical systems by the publication of a paper by Bose on Planck's radiation formula. The novelty lay in Bose's modification of those steps in statistical theory which are concerned with *a priori* probability. Yet so far is it true to say there is "nothing new under the sun" that we can find the germ of Bose's idea in Planck's earliest papers on black body radiation, and it will prove serviceable to refresh one's memory on the discussion in section 14.2. In the traditional methods of statistical theory each particle (molecule, atom, electron) in a system is assumed to have a recognisable individuality, and in this way one complexion is distinguished from another even if they are embraced in the same state of numerical distribution of the particles between the phase-cells. In section 14.2, however, we considered complexions as settled by the distribution of elements of energy among the particles, and this led to the substitution of an expression such as

$$\frac{(n + c - 1)!}{n! (c - 1)!}$$

for the value of a probability W instead of the usual

$$\frac{n!}{n_1! n_2! \dots n_c!}.$$

It is expressions of the former type which enter into Bose's analysis and link it up with Planck's earlier treatment.

4. *Bose's Statistics of Light Quanta in a Temperature-Enclosure.*—In his work Bose regards radiation as composed of light-quanta, or particles with energy $h\nu$ where ν is the frequency of the quantum. In accordance with present views as to matter and energy, a particle is regarded as having mass $h\nu/c^2$ * and momentum $h\nu/c$ where c is the

* *I.e.*, mass at velocity c ; their "rest-mass" is zero, according to Relativity theory.

velocity of light. Each light-quantum is represented in a six-dimensional phase-diagram representing position (x, y, z) and momentum (ξ, η, ζ). Of course

$$\xi^2 + \eta^2 + \zeta^2 = (h\nu/c)^2.$$

If we integrate $dx dy dz d\xi d\eta d\zeta$ throughout the region of the phase-diagram in which the energy is not greater than $h\nu$ where ν is a particular frequency we obtain

$$v \frac{4\pi}{3} \left(\frac{h\nu}{c} \right)^3$$

where v is the volume of the enclosure containing the radiation. In this region of phase-extension no points representing quanta of higher frequency than ν can occur.

In the extension

$$\frac{4\pi v h^3}{c^3} \nu^2 \delta\nu$$

will occur these points which represent quanta with frequencies between ν and $\nu + \delta\nu$. If we now introduce the assumption that the elementary phase-cells have the magnitude h^3 , then the number of the cells in the shell bounded by the frequencies ν and $\nu + \delta\nu$ is

$$\frac{4\pi v}{c^3} \nu^2 \delta\nu.$$

The problem is to determine the distribution of the numbers of light-quanta among the various frequencies in an enclosure of volume v containing full radiation, *i.e.*, radiation in temperature equilibrium with the walls of the enclosure. This condition determines the amount of energy in the radiation, but it does not determine the total number of light-quanta present. We cannot assign an unchanging individuality to any light-quantum in the enclosure, since the walls are emitting and absorbing radiation; even the number in the radiation is not necessarily unchangeable; for if a quantum of frequency ν is absorbed by the wall it can be replaced by emission of several quanta of frequencies, ν', ν'', \dots without any breach of the energy condition, provided ν is equal to the sum of ν', ν'', \dots . Conceive the

whole range of frequencies to be divided into elementary ranges between the frequencies $\nu_1, \nu_2, \dots \nu_r$, etc. . . . where we can write $\delta\nu_r$ for $\nu_r - \nu_{r-1}$. Suppose the total number of light quanta in the radiation at any moment to be n , and that of these n_1 lie in the range o to ν_1 , n_2 in the range ν_1 to ν_2 , . . . n_r in the range ν_{r-1} to ν_r , etc. We have to find the number of complexions which corresponds to this numerical distribution among the elementary ranges. It is here that Bose resorts to the earlier method of Planck. Take, for instance, the n_r quanta in the range ν_{r-1} to ν_r . Their representative points lie in a shell of the phase-diagram which is constituted of a_r elementary phase-cells where

$$a_r = \frac{4\pi\nu}{c^3} \nu_r^2 \delta\nu_r \quad . \quad . \quad . \quad . \quad (I.1).$$

As we have seen in section 14.2 there are

$$\frac{(n_r + a_r - 1)!}{n_r! (a_r - 1)!} \quad . \quad . \quad . \quad . \quad (I.2)$$

different ways of partitioning the n_r light-quanta among the cells when we disregard individuality of the quanta. The formula, in fact, goes back to (2.5) as it gives the number of actual terms in the expansion of

$$(x_1 + x_2 + \dots x_b)^p$$

where for the moment we are writing b for a_r and p for n_r . The coefficient

$$\frac{p!}{p_1! p_2! \dots p_b!}$$

of a term such as $x_1^{p_1} x_2^{p_2} \dots x_b^{p_b}$ is disregarded. It entered into the earlier work because we assumed that each particle had a recognisable individuality. Now we regard the term $x_1^{p_1} x_2^{p_2} \dots x_b^{p_b}$ just as representing one way of partitioning of p light-quanta among the b cells, and there are just $(p + b - 1)!/[p! (b - 1)!]$ such terms, *i.e.*, ways of partitioning.

Expressions similar to (I.2) give the number of ways of partitioning the n_1 light-quanta among the a_1 cells of the

range 0 to ν_1 , the n_2 light-quanta among the a_2 cells of range ν_1 to ν_2 , and so on. Any combination of special ways of partitioning in the separate shells gives one way of partitioning the total n light-quanta over the whole phase-diagram. Hence the total number of ways of distributing n light-quanta is on this view of the matter equal to the product of the terms such as (I . 2) ; *i.e.*, it is

$$\prod \frac{(n_r + a_r - 1)!}{n_r! (a_r - 1)!} \quad . \quad . \quad . \quad . \quad (I.3)$$

where

$$\sum n_r = n,$$

and each a_r is defined by (I . 1).

There is, of course, the energy condition to be satisfied, *viz.*,

$$\sum n_r h\nu_r = E \quad . \quad . \quad . \quad . \quad (I.4)$$

where E is a constant ; *but there is no constant n condition.* The problem is now to find the values of $n_1, n_2, \dots, n_r, \dots$ which make (I . 3) a maximum subject to the *one* condition (I . 4). The procedure is the familiar one. Calling (I . 3) $W(n, a)$, we take its logarithm, use Stirling's theorem, and apply the variational method.

So we have to solve

$$\delta \{ \sum (n_r + a_r) \log (n_r + a_r) - n_r \log n_r - a_r \log a_r \} = 0^*$$

subject to

$$\nu_r \delta n_r = 0.$$

Thus using an undetermined multiplier α we easily find that for each value of the integer r

$$\log (n_r + a_r) - \log n_r - \alpha \nu_r = 0$$

and so

$$\frac{n_r + a_r}{n_r} = \exp (\alpha \nu_r)$$

or

$$n_r = \frac{a_r}{\exp (\alpha \nu_r) - 1} \quad . \quad . \quad . \quad . \quad (I.5).$$

Equations (I . 1) and (I . 4) will then determine α as a function of E and ν ; for (I . 1) shows that

$$n_r = \frac{4 \pi \nu}{c^3} \frac{\nu_r^2 \delta \nu_r}{\exp (\alpha \nu_r) - 1}.$$

* We can drop out minus unity as negligible.

It follows that

$$\frac{E}{v} = \Sigma \frac{4\pi h}{c^3} \cdot \frac{\nu_r^3 \delta \nu_r}{\exp(\alpha \nu_r) - 1}$$

or going to the limit we find for the energy density

$$\frac{4\pi h}{c^3} \int_0^\infty \frac{\nu^3 d\nu}{\exp(\alpha \nu) - 1}.$$

In this reasoning we have omitted, so far, any reference to one point which will be familiar to those acquainted with optical theory, and which has made its appearance in these pages in Chapter XXII. It is the matter of polarisation of light. The effect of allowing for this is to double the above result and make it

$$\frac{8\pi h}{c^3} \int_0^\infty \frac{\nu^3 d\nu}{\exp(\alpha \nu) - 1}.$$

To find α in terms of the temperature θ of the enclosure we introduce the usual expression for the entropy, *viz.*, $k \log W_m$, where

$$\log W_m = \Sigma \left[(n_r + a_r) \log (n_r + a_r) - n_r \log n_r - a_r \log a_r \right]$$

the n_r having the values given by (I. 5). If we now raise the temperature the energy of the radiation increases to $E + \delta E$, and there is a corresponding increase of entropy from S to $S + \delta S$. The limit of $\delta S / \delta E$ is θ^{-1} , since the volume v of the enclosure is maintained constant, and no external work is done by the pressure of the radiation. Writing ϵ_r for $h\nu_r$ and μ for α/h we have

$$\begin{aligned} S &= k \Sigma \left\{ (n_r + a_r) \log (n_r + a_r) - n_r \log n_r - a_r \log a_r \right\} \\ &= k \Sigma \left\{ (n_r + a_r) (\log n_r + \alpha \nu_r) - n_r \log n_r - a_r \log a_r \right\} \\ &= k \Sigma \left\{ a_r (\log n_r - \log a_r) + (n_r + a_r) \mu \epsilon_r \right\} \\ &= k \Sigma \left\{ -a_r \log [\exp(\mu \epsilon_r) - 1] + a_r \mu \epsilon_r + n_r \mu \epsilon_r \right\} \\ &= k \Sigma \left\{ a_r (\mu \epsilon_r - \log [\exp(\mu \epsilon_r) - 1]) \right\} + k \mu E \\ &= k \left\{ \mu E - \Sigma a_r \log [1 - \exp(-\mu \epsilon_r)] \right\}. \end{aligned}$$

So it follows that

$$\begin{aligned}
 \theta &= \frac{dS}{dE} \\
 &= k\mu + kE \frac{d\mu}{dE} - k \Sigma \left\{ a_r \frac{d \log [1 - \exp (-\mu \epsilon_r)]}{dE} \right\} \\
 &= k\mu + kE \frac{d\mu}{dE} - k \Sigma \left\{ \frac{a_r}{1 - \exp (-\mu \epsilon_r)} \exp (-\mu \epsilon_r) \epsilon_r \frac{d\mu}{dE} \right\} \\
 &= k\mu + kE \frac{d\mu}{dE} - k \Sigma \left(\frac{a_r \epsilon_r}{\exp (\mu \epsilon_r) - 1} \right) \frac{d\mu}{dE} \\
 &= k\mu + kE \frac{d\mu}{dE} - k \Sigma (n_r \epsilon_r) \frac{d\mu}{dE} \\
 &= k\mu
 \end{aligned}$$

and thus μ has its usual value, viz., $(k\theta)^{-1}$. So we arrive ultimately at Planck's expression for the energy-density in the temperature-enclosure, E/v , viz.,

$$\frac{8 \pi h}{c^3} \int_0^\infty \frac{\nu^3 d\nu}{\exp (h\nu/k\theta) - 1}.$$

II. *Einstein's Theory of an Ideal Gas.*—The method of Bose is therefore justified by its success. Einstein immediately applied the same method to the discussion of a monatomic gas. The region of the phase-diagram in which will fall all the points representing any molecule whose energy does not exceed the value ϵ is given by integrating $dx dy dz d\xi d\eta d\zeta$ throughout a range of values determined by the volume v of the vessel and the condition

$$\xi^2 + \eta^2 + \zeta^2 \leq 2m\epsilon.$$

Its magnitude is

$$\frac{v 4 \pi}{3} (2m\epsilon)^{\frac{3}{2}}.$$

The region in which lie the points corresponding to molecules whose energies lie between ϵ and $\epsilon + \delta\epsilon$ is thus

$$2 \pi v (2m)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} \delta\epsilon,$$

and the number of elementary phase-cells in this region is thus

$$\frac{2 \pi v (2m)^{\frac{3}{2}}}{h^3} \epsilon^{\frac{1}{2}} \delta\epsilon.$$

As before, we divide the phase-diagram into shells by the energy-hypersurfaces corresponding to $\epsilon_1, \epsilon_2, \dots, \epsilon_r, \dots$ and write $\epsilon_r - \epsilon_{r-1} = \delta\epsilon_r$. The number of cells in the shell bounded by ϵ_{r-1} and ϵ_r is a_r where

$$a_r = \frac{2 \pi v (2 m)^3}{h^3} \epsilon_r^{\frac{1}{2}} \delta\epsilon_r \quad . \quad . \quad . \quad (II.1).$$

The partitioning is carried out as above, and the number of complexions corresponding to an energy content of the gas equal to E is $W(n, a)$, *i.e.*, expression (I. 3) where

$$\sum n_r \epsilon_r = E.$$

But, of course, we have now the condition to satisfy that

$$\sum n_r = n = \text{constant},$$

for although we disregard individuality of molecules in counting complexions, we must remember that in this case no particles are created or destroyed. When we take the logarithm of $W(n, a)$, vary it, put the variation equal to zero and take account of

$$\sum \epsilon_r \delta n_r = 0$$

and

$$\sum \delta n_r = 0$$

we obtain

$$\log(n_r + a_r) - \log n_r = \lambda + \mu \epsilon_r,$$

involving two undetermined constants as usual. Thus

$$n_r = \frac{a_r}{\exp(\lambda + \mu \epsilon_r) - 1} \quad . \quad . \quad . \quad (II.2)$$

where, of course, a_r is given by (II. 1).

The entropy S is $k \log W_m$ where W_m is the value of $W(n, a)$ with this expression for n_r inserted. It is easily shown as above that it is given by

$$S = k \left\{ n\lambda + \mu E - \sum a_r \log [1 - \exp(-\lambda - \mu \epsilon_r)] \right\} \quad (II.3).$$

On working out dS/dE as above, we find, as before, that the constant μ is connected with the temperature θ by the usual result. Putting in the values for the a_r it follows,

after a step or two, that the number of molecules whose energies lie in the range ϵ to $\epsilon + \delta\epsilon$ is given by

$$\frac{2 \pi v (2 m)^{\frac{3}{2}}}{h^3} \frac{\epsilon^{\frac{1}{2}}}{e^{\lambda + \mu \epsilon} - 1} \delta\epsilon \quad . \quad . \quad . \quad (\text{II} . 4)$$

where the constant λ is determined by the condition

$$n = \frac{2 \pi v (2 m)^{\frac{3}{2}}}{h^3} \int_0^{\infty} \frac{\epsilon^{\frac{1}{2}}}{e^{\lambda + \mu \epsilon} - 1} d\epsilon.$$

The result (II . 4) replaces the Maxwell Boltzmann law, to which it clearly reduces in case where unity is negligible in comparison with $\exp(\lambda + \mu\epsilon)$. Further it easily follows that

$$E = \frac{2 \pi v (2 m)^{\frac{3}{2}}}{h^3} \int_0^{\infty} \frac{\epsilon^{\frac{3}{2}}}{e^{\lambda + \mu \epsilon} - 1} d\epsilon \quad . \quad . \quad (\text{II} . 5)$$

and

$$S = R\lambda + \frac{E}{\theta} - \frac{2 \pi v (2 m)^{\frac{3}{2}} k}{h^3} \int_0^{\infty} \epsilon^{\frac{1}{2}} \log (1 - e^{-\lambda - \mu \epsilon}) d\epsilon \quad (\text{II} . 6).$$

III. *The Fermi-Dirac Statistics.*—This change in the manner of counting complexions was suggested, as we have said, just on the eve of the third period in the history of quantum ideas. About the same time a suggestion was made by Pauli in connection with the Bohr theory of atom structure, which is called Pauli's exclusion principle; it concerns the description of the quantum paths of the electrons in an atom in terms of quantum numbers, and postulates that in a given atom or molecule no two electrons can have the same set of quantum numbers, *i.e.*, that at any instant two electrons cannot be on the same quantum orbit. In statistical theory we have seen already the analogy of quantum paths of representative points and phase-cells, and in 1926 Fermi suggested that in dealing with the statistics of systems of molecules we should reckon up the complexions on an analogous exclusion principle, *viz.*, that complexions in which two or more representative points occupied one energy cell should be ruled out as impossible. Independently, Dirac made the same sugges-

tion, and also showed how it could be regarded as a reasonable conclusion from the new quantum mechanics, which was just about a year old at the time, and which had also produced a theoretical justification of the original Pauli exclusion principle concerning electrons in atoms. The effect of this on the formulæ of statistical theory is not hard to discover. Like Bose and Einstein, Fermi and Dirac abandon any idea of individualising molecules, but concentrate, as it were, on the individuality of the elementary phase-cells in an "energy-shell" of the phase-diagram. For Bose and Einstein the occurrence of any number of representative points in a cell was as likely as the occurrence of any other; for Fermi and Dirac this is not so; a cell can contain one point or none; each alternative is equally likely; but it is impossible that it should contain two or more. The earlier results of Section II. are simply repeated, *viz.*,

$$a_r = \frac{2 \pi v (2m)^{\frac{3}{2}}}{h^3} \epsilon_r^{\frac{1}{2}} \delta \epsilon_r \quad . \quad . \quad . \quad (\text{III. 1})$$

where

$$\Sigma n_r \epsilon_r = E$$

and

$$\Sigma n_r = n.$$

But instead of taking $W(n, a)$ as given by (I. 3), it is determined by

$$W(n, a) = \Pi \frac{a_r!}{n_r! (a_r - n_r)!} \quad . \quad . \quad (\text{III. 2})$$

for the number of ways of arranging n things in a boxes on the understanding that no box is to hold more than one thing is just the number of combinations of a things taken n at a time. The algebraic procedure now follows similar lines, and produces these results

$$n_r = \frac{a_r}{\exp(\lambda + \mu \epsilon_r) + 1} \quad . \quad . \quad (\text{III. 3})$$

$$S = k \log W_m$$

$$= k \{ n\lambda + \mu E + \Sigma a_r \log [1 + \exp(-\lambda - \mu \epsilon_r)] \} \quad (\text{III. 4})$$

and, dS/dE being put equal to θ^{-1} , we find the usual result

for μ . The Fermi-Dirac law of distribution replacing the Maxwell-Boltzmann law now turns out to be

$$\frac{2 \pi v (2 m)^{\frac{3}{2}}}{h^3} \frac{\epsilon^{\frac{1}{2}}}{e^{\lambda + \mu \epsilon} + 1} \delta \epsilon \quad . \quad . \quad . \quad (\text{III} . 4)$$

with λ determined by

$$n = \frac{2 \pi v (2 m)^{\frac{3}{2}}}{h^3} \int_0^{\infty} \frac{\epsilon^{\frac{1}{2}}}{e^{\lambda + \mu \epsilon} + 1} d\epsilon.$$

Also

$$E = \frac{2 \pi v (2 m)^{\frac{3}{2}}}{h^3} \int_0^{\infty} \frac{\epsilon^{\frac{3}{2}}}{e^{\lambda + \mu \epsilon} + 1} d\epsilon \quad . \quad (\text{III} . 5)$$

and

$$S = R\lambda + \frac{E}{\theta} + \frac{2 \pi v (2 m)^{\frac{3}{2}} k}{h^3} \int_0^{\infty} \epsilon^{\frac{1}{2}} \log (1 + e^{-\lambda - \mu \epsilon}) d\epsilon \quad (\text{III} . 6).$$

The change from minus unity to plus unity is, of course, a negligible affair under conditions where the Maxwell-Boltzmann law is a justifiable approximation, but, as we shall see in a moment, it is quite otherwise under more unusual conditions. But even when the Maxwell-Boltzmann law is a good approximation the new statistical theory produces the value of the entropy constant in a very direct and easy manner. Thus if we neglect the ± 1 we obtain

$$n = \gamma e^{-\lambda} \int_0^{\infty} \epsilon^{\frac{1}{2}} e^{-\mu \epsilon} d\epsilon,$$

where γ is written for $2 \pi v (2m)^{\frac{3}{2}}/h^3$, and so writing x^2 for $\mu \epsilon$ and using the familiar results for $\int_0^{\infty} x^r e^{-x^2} dx$ we find

$$n = \gamma e^{-\lambda} \pi^{\frac{1}{2}} (k\theta)^{\frac{3}{2}}/2,$$

so that

$$e^{\lambda} = \frac{v}{nh^3} (2 \pi m k \theta)^{\frac{3}{2}} \quad . \quad . \quad . \quad (\text{III} . 7).$$

For hydrogen under normal conditions this gives 6×10^4 for λ , and so justifies the approximation used, but if v or θ are very small, *i.e.*, at large densities or low temperatures, λ is too small to permit the neglect of the unity term. Pro-

ceeding, however, under the suitable conditions we find that

$$\begin{aligned} E &= \gamma e^{-\lambda} \int_0^{\infty} \epsilon^{\frac{3}{2}} e^{-\mu \epsilon} d\epsilon \\ &= \gamma e^{-\lambda} 3 \pi^{\frac{1}{2}} (k\theta)^{\frac{3}{2}}/4, \end{aligned}$$

and so

$$\frac{E}{n} = \frac{3 k\theta}{2}$$

the familiar energy-partition law.

$$\text{Hence} \quad S = R\lambda + \frac{E}{\theta} + k\gamma e^{-\lambda} \int_0^{\infty} \epsilon^{\frac{1}{2}} e^{-\mu \epsilon} d\epsilon,$$

remembering that $\log (1 \pm x) = \pm x$ if x is sufficiently small compared to unity. Thus

$$\begin{aligned} S &= R\lambda + \frac{E}{\theta} + kn \\ &= R(\lambda + 1) + \frac{3}{2}R \\ &= R\left(\lambda + \frac{5}{2}\right) \end{aligned}$$

$$\text{by III . 7} = R \left[\log v - \log n - 3 \log h + \frac{3}{2} \log (2 \pi m k) \right. \\ \left. + \frac{3}{2} \log \theta + \frac{5}{2} \right]$$

$$= R \left[\frac{5}{2} \log \theta - \log p + \frac{5}{2} + \log \frac{(2 \pi m k)^{\frac{3}{2}} k}{h^3} \right]$$

(III . 8)

where p is written for $nk\theta$ as usual.

To decide between the two results one must consider conditions under which the unity term is not negligible, and then experimental evidence leans towards the Fermi-Dirac result, and so supports the conclusions of the new quantum mechanics. The trouble with the Einstein result is that while it makes the entropy of a gas tend to zero as the temperature decreases to zero (thus extending the Planck-Nernst heat law to all substances, condensed or not), it makes the specific heat first rise to a maximum and then decrease to zero asymptotically. Now this maximum property has not been observed for any gas, and

so the Einstein-Bose statistical theory lacks support in that particular. On the other hand, with the Fermi-Dirac statistics, it can be shown that *at low temperatures*

$$E = E_0 + \alpha \theta^2$$

where

$$E_0 = \frac{3}{40} \left(\frac{6n}{\pi v} \right)^{\frac{1}{2}} \frac{nh^2}{m}$$

and

$$\alpha = 2 \left(\frac{\pi v}{9n} \right)^{\frac{1}{2}} \frac{m}{nh^2} \pi^2 n^2 k^2$$

so that the specific heat $2 \alpha \theta$ approaches zero as a limit without any intervening maximum. It is clear also that the Fermi-Dirac statistics necessitates a nul-point energy ; this is evident from the fundamental postulate, for of all the molecules whose representative points fall within a group of phase-cells which have one volume-element in common only one can be in that phase-cell of the group which corresponds to zero velocity. All the others will fall into cells with as small energy as possible, but up to a certain limit each cell will have one point in it. In the Einstein-Bose statistics the constant λ is essentially positive, and has zero as its limiting value ; this is obvious from result (II. 4) ; otherwise n_r would be negative for small enough values of ϵ . At the limit $\lambda = 0$ all the representative points would crowd into the cell of lowest energy, since $1/(e^{\epsilon} - 1)$ is infinite for the zero value of ϵ . This is an extreme case of what is called "degeneracy." So as λ decreases, either with decreasing temperature or increasing density, the system passes from the classical Maxwell-Boltzmann distribution to a state of extreme degeneracy ; and for small values of λ particles with a low velocity are present in greater numbers than is the case of a classical distribution with the same density and temperature. In the Fermi-Dirac statistics, on the other hand, λ may have positive or negative values.* The distribution differs markedly from the classical when $v (2 \pi m k \theta)^{\frac{3}{2}} / (n h^3)$ is much less than unity ; λ is then large and *negative*, thus making

* *N.B.*—The values of λ are not necessarily the same for the three cases, even when density and temperature are the same.

$e^{\lambda+\mu\epsilon}$ small compared with unity, except for very large values of ϵ . This means that for a large range of ϵ , $n_r = a_r$, (see III. 3), or every cell has one representative point in it. The system is degenerate. In cases of degeneracy the Fermi-Dirac statistics implies that molecules with low velocities occur in greater number than in a classical distribution at the same temperature and density.

The reader should for further information consult a paper by Lennard-Jones in the *Proc. Phys. Soc.* (London), Vol. XL., Part 5, (August, 1928), where a full bibliography of papers on these matters will also be found.

IX. *The Statistical Method of Darwin and Fowler. Partition Functions.*—An innovation of a different character has been introduced lately by Darwin and Fowler. The original papers are to be found in the *Phil. Mag.*, Vol. XLIV., Nos. 261, 263 (September, November, 1922). They begin by pointing out the weak spot in the practical working out of the statistical calculations on the usual lines, *viz.*, the use of Stirling's Theorem. This point is not always brought home in current accounts. Let us, for example, consider a gram-molecule of a gas under standard conditions with a volume about 20 litres. The energy is $1.5 R\theta$, about 3×10^{10} ergs. If this were all in one molecule its momentum would be $(1.5 Rm\theta)^{\frac{1}{2}}$, about 10^{-7} grammem, for hydrogen. Thus the whole momentum extension would be of the order 10^{-20} in the phase-diagram, and when associated with the volume 20 litres, the phase-extension of the phase-diagram actually required for a gram-molecule of hydrogen at ordinary temperatures and pressures would be of the order 10^{-16} (erg-sec.)³. Suppose this is now divided into elementary cells, h^3 each having, therefore, an extension of the order 10^{-79} . There are 10^{63} such cells in the whole extension. But there are only about 10^{24} representative points to partition among them! But the use of Stirling's theorem quietly assumes that in practice the points available are much more numerous than the cells.

Of course, on purely classical lines we can retort that we are not compelled, in order to arrive at the classical result, to postulate cells as small as Planck's element. Still the

use of that element in quantum discussions of the "classical-quantum" type requires subsequent justification of the results.

Darwin and Fowler show that this rather illegitimate use of Stirling's theorem can be avoided entirely by considering the *average* state of a system, rather than its "most probable," as the analogue of the state of thermodynamic equilibrium. In practice this leads to no new result, but the point of view and method are quite different. We can illustrate this by a simple example. Suppose we have present a set of Planck vibrators which each contain a multiple of a unit of energy ϵ . Let there be n vibrators and an amount of energy E available where E/ϵ is an *integer*. Let us consider a complexion in which there are n_0 vibrators with no energy, n_1 with ϵ , n_2 with 2ϵ , etc. There are as usual

$$\frac{n!}{n_0! n_1! n_2! \dots}$$

complexions in a corresponding statistical state, and we have to satisfy the conditions

$$\begin{aligned} n_0 + n_1 + n_2 + n_3 + \dots &= n \\ n_1 + 2n_2 + 3n_3 + \dots &= E/\epsilon \end{aligned} \quad (\text{IV. 1}).$$

Let C be the total number of complexions compatible with these conditions. C will be given by

$$C = \sum \frac{n!}{n_0! n_1! n_2! \dots}$$

where the summation is over all possible values of the n which satisfy (IV. 1). If we consider the series

$$(1 + z + z^{2\epsilon} + z^{3\epsilon} + \dots)^n \quad (\text{IV. 2})$$

the typical term is

$$\frac{n!}{n_0! n_1! n_2! \dots} z^{(n_1 + 2n_2 + 3n_3 + \dots)\epsilon}$$

where the n_r satisfy (IV. 1). Thus if we pick out the coefficient of z^E in the expansion (IV. 2) we shall have the value of C . So C is the coefficient of z^E in $(1 - z^\epsilon)^{-n}$,

i.e., of y^c in $(1 - y)^{-n}$ where $c = E/\epsilon$. But by the binomial theorem

$$(1 - y)^{-n} = 1 + ny + \frac{n(n+1)}{1 \cdot 2} y^2 + \frac{n(n+1)(n+2)}{1 \cdot 2 \cdot 3} y^3 + \\ + \frac{(n+c-1)!}{(n-1)! c!} y^c + \dots$$

and so

$$C = \frac{(n+c-1)!}{(n-1)! c!}$$

a result which we have already met several times.

The average value of any quantity denoted by u can then be determined by the equation

$$C \bar{u} = \Sigma \frac{n!}{n_0! n_1! n_2! \dots} u z^{(n_1 + 2n_2 + 3n_3 + \dots)\epsilon} \quad (\text{IV } 3).$$

Thus the average value of the energy is given by

$$C \bar{E} = \Sigma \frac{n!}{n_0! n_1! n_2! \dots} \epsilon (n_1 + 2n_2 + 3n_3 + \dots) z^{(n_1 + 2n_2 + 3n_3 + \dots)\epsilon} \\ = z \frac{d}{dz} (1 + z^\epsilon + z^{2\epsilon} + z^{3\epsilon} + \dots)^n \\ = z \frac{d}{dz} \frac{1}{(1 - z^\epsilon)^n} \\ = \frac{\epsilon n z^\epsilon}{(1 - z^\epsilon)^{n+1}} \\ = - \frac{1}{(1 - z^\epsilon)^n} \left[n z \frac{d}{dz} \log (1 - z^\epsilon) \right] \quad (\text{IV } 4).$$

The expression (IV . 4) is obtained so as to render possible a method of approximate calculation which discards Stirling's theorem and uses the method of "contour integration." * In this z is regarded as a complex variable, and by integrating round a circle in the Argand diagram with the origin as centre, and a radius less than unity, we know that

$$C = \frac{1}{2\pi i} \int \frac{dz}{z^{E+1}} \frac{1}{(1 - z^\epsilon)^n},$$

* See Jefferies' *Operational Methods in Physics* (Camb. Math. Tracts).

and

$$C \bar{E} = \frac{1}{2\pi i} \int \frac{dz}{z^{E+1}} \frac{-nz \frac{d}{dz} \log(1-z^e)}{(1-z^e)^n} \quad . \quad . \quad (IV. 5).$$

These expressions are *exact*, but in the theory of contour-integrals there is a method known as the “method of steepest descents” which leads to simple approximations that are adequate and rigorous under certain conditions satisfied in most problems. The process is this:—

The integrands being infinite at $z = 0$, and also at $z = 1$, there must be a minimum value of the integrand at some point on the positive axis where $z = \vartheta$ (ϑ is of course, a *real* number less than unity). Now take the circular contour round which the integration is effected to be a circle of radius ϑ . It can be shown that *as we travel along this circle* the values of the integrands have strong maxima at $z = \vartheta$ and drop to relatively very small values at all points on the contour outside the very short arc containing the point $z = \vartheta$. Lest there be any confusion on the part of the reader about these statements, let him note that the value of an integrand at $z = \vartheta$ is a minimum for all the values at points on the real axis between $z = 0$ and $z = 1$. But it is maximum for the values at points along the circle. Indeed, if n and E are large enough this maximum is so strong that practically the whole of the contour integral is contributed by a short arc of the circle in the neighbourhood of $z = \vartheta$. Under these circumstances we can remove the term $nz(d/dz) \log(1-z^e)$ outside the integral sign provided z is given the value ϑ .

This value ϑ is thus obtained by solving the equation

$$\frac{d}{dz} \frac{1}{z^{E+1} (1-z^e)^n} = 0,$$

or practically

$$\frac{d}{dz} \frac{1}{z^E (1-z^e)^n} = 0.$$

This equation is easily seen to be

$$E(1-z^e) - n\epsilon z^e = 0,$$

so that ϑ is given by

$$E = \frac{n\epsilon}{\vartheta^{-\epsilon} - 1} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (IV.6).$$

We then have, owing to these approximations

$$C = \frac{A}{\vartheta^{E+1} (1 - \vartheta^\epsilon)^n}$$

$$C \bar{E} = \frac{-A n \vartheta \frac{d}{d\vartheta} \log (1 - \vartheta^\epsilon)}{\vartheta^{E+1} (1 - \vartheta^\epsilon)^n},$$

where A is some constant.

So that

$$\bar{E} = -n\vartheta \frac{d}{d\vartheta} \log (1 - \vartheta^\epsilon)$$

$$= \frac{n\epsilon}{\vartheta^{-\epsilon} - 1} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (IV.7).$$

Now, of course, this result is entirely trivial in this case. As we assumed that the energy of the system is constant, obviously the average energy of the system over all the complexions is just the constant energy for each complexion, as (IV.6) and (IV.7) show. The example, however, is the easiest illustration of the process of approximation employed. Let us choose one which does not lead to a trivial result, *viz.*, a system which consists of a vibrators with a fundamental quantum energy ϵ , and b vibrators with a fundamental quantum η . For the purposes of the calculation we must assume that ϵ and η are commensurable, but it does not matter how large are the integers which are required to express ϵ/η in its lowest terms. We may, of course, choose the unit of energy so that ϵ and η are themselves integers. The number of complexions embraced in a state in which a_r vibrators of the first type have an energy $r\epsilon$ and b_s vibrators of the second type have an energy $s\eta$ is

$$\frac{a!}{a_0! a_1! a_2! \dots} \cdot \frac{b!}{b_0! b_1! b_2! \dots} \quad \cdot \quad \cdot \quad (IV.8)$$

where we must satisfy the conditions

$$\begin{aligned}\Sigma a_r &= a \\ \Sigma b_s &= b \\ \Sigma (ra_r \epsilon + sb_s \eta) &= E \quad . \quad . \quad . \quad (IV.9).\end{aligned}$$

The total number of complexions possible with the energy E is as before

$$C = \Sigma \frac{a!}{a_0! a_1! a_2! \dots} \cdot \frac{b!}{b_0! b_1! b_2! \dots} \quad (IV.10)$$

where the summation is over all values of the a_r and b_s compatible with (IV.9). Now the whole energy E can be considered as made up of two parts, E_a and E_b , one the energy in all the vibrators of the first type, the other in those of the second type. The average value of E_a over all the complexions is given by

$$C \bar{E}_a = \Sigma \frac{(a_1 + 2a_2 + 3a_3 + \dots)\epsilon \cdot a! b!}{a_0! a_1! a_2! \dots b_0! b_1! b_2! \dots} \quad (IV.11).$$

As before, we can easily show that C is the coefficient of z^E in

$$\frac{1}{(1 - z^\epsilon)^a (1 - z^\eta)^b}$$

and $C \bar{E}_a$ is the coefficient of z^E in

$$\frac{1}{(1 - z^\eta)^b} z \frac{d}{dz} \frac{1}{(1 - z^\epsilon)^a}$$

or

$$-\frac{1}{(1 - z^\eta)^b} \frac{a z \frac{d}{dz} \log(1 - z^\epsilon)}{(1 - z^\epsilon)^a}.$$

This leads to the following contour integrals for C and $C \bar{E}_a$

$$\begin{aligned}C &= \frac{1}{2\pi i} \int \frac{dz}{z^{E+1}} \frac{1}{(1 - z^\epsilon)^a (1 - z^\eta)^b} \\ C \bar{E}_a &= -\frac{1}{2\pi i} \int \frac{dz}{z^{E+1}} \frac{a z \frac{d}{dz} \log(1 - z^\epsilon)}{(1 - z^\epsilon)^a (1 - z^\eta)^b}.\end{aligned}$$

There is a strong maximum for the integrands in a small arc at $z = \vartheta$ of the contour circle of radius ϑ where ϑ is determined by

$$\frac{d}{dz} \frac{1}{z^{E+1} (1-z^\epsilon)^a (1-z^\eta)^b} = 0$$

so that ϑ is found from the equation

$$E = \frac{a\epsilon}{\vartheta^{-\epsilon} - 1} + \frac{b\eta}{\vartheta^{-\eta} - 1} \quad . \quad . \quad (IV. 12).$$

This leads to the approximation

$$C = \frac{A}{\vartheta^{E+1} (1-\vartheta^\epsilon)^a (1-\vartheta^\eta)^b}$$

$$C \bar{E}_a = - \frac{Aa\vartheta \frac{d}{d\vartheta} \log (1-\vartheta^\epsilon)}{\vartheta^{E+1} (1-\vartheta^\epsilon)^a (1-\vartheta^\eta)^b}$$

leading to

$$\bar{E}_a = -a\vartheta \frac{d}{d\vartheta} \log (1-\vartheta^\epsilon)$$

$$= \frac{a\epsilon}{\vartheta^{-\epsilon} - 1} \quad . \quad . \quad . \quad . \quad (IV. 13)$$

similarly,

$$\bar{E}_b = \frac{b\eta}{\vartheta^{-\eta} - 1}.$$

This determines the average partition of the energy between the two types of oscillators. The method can obviously be extended to any number of different types. We have to identify the quantity ϑ with the usual properties of the system. It is fairly evident that it is connected with the temperature, and if we take the temperature on the absolute thermodynamic scale to be the same as that defined by the equipartition law for systems following the classical dynamical principles, we can find what ϑ is. Thus suppose that the second type of vibrators have a low frequency and a small value of η . In the limit they follow the classical laws, and $\vartheta^{-\eta}$ is nearly unity. If it is a little greater than unity

$$\log [1 + (\vartheta^{-\eta} - 1)] \doteq \vartheta^{-\eta} - 1$$

$$\text{or} \quad \vartheta^{-\eta} - 1 = -\eta \log \vartheta,$$

$$\text{so that} \quad \frac{\eta}{\vartheta^{-\eta} - 1} \doteq \frac{1}{\log (1/\vartheta)}.$$

If $\vartheta^{-\eta}$ is a little less than unity

$$\log [1 - (1 - \vartheta^{-\eta})] = -(1 - \vartheta^{-\eta}),$$

and the same result follows. Thus in the limit the particles of a system obeying classical laws have each an average energy, $\log (1/\vartheta)$. This is, of course, kinetic and potential, and is $k\theta$, so that

$$\vartheta = e^{-\mu}$$

where μ is $(k\theta)^{-1}$, and we arrive at the usual Planck law of partition among the oscillators of the first type, *viz.*,

$$\overline{E}_a = \frac{a\epsilon}{e^{\mu\epsilon} - 1}.$$

A generalisation to more general types can be easily made. Suppose that particles of type 1, a in number, can be in states for which the energies are $\epsilon_1, \epsilon_2, \epsilon_3$, etc. ; particles of type 2, b in number, can be in states for which the energies are $\eta_1, \eta_2, \eta_3, \dots$ and so on. Further, we may suppose that several quantum states belong to one energy state, so that the states of type 1 particles have weights p_1, p_2, p_3, \dots respectively, of type 2 particles, q_1, q_2, q_3, \dots respectively, and so on. The weighted number of complexions which correspond to an assigned specification is

$$\frac{a!}{a_1! a_2! \dots} p_1^{a_1} p_2^{a_2} \dots \frac{b!}{b_1! b_2! \dots} q_1^{b_1} q_2^{b_2} \dots$$

where

$$\Sigma a_r = a$$

$$\Sigma b_s = b$$

$$\dots$$

$$\Sigma a_r \epsilon_r + \Sigma b_s \eta_s + \dots = E.$$

The functions

$$\phi(z) = p_1 z^{\epsilon_1} + p_2 z^{\epsilon_2} + p_3 z^{\epsilon_3} + \dots$$

$$\psi(z) = q_1 z^{\eta_1} + q_2 z^{\eta_2} + q_3 z^{\eta_3} + \dots$$

take the place of $(1 - \epsilon)^{-1}, (1 - \eta)^{-1}$, etc., in the previous

example. They are called the "partition functions" of the corresponding types of particles. Proceeding as before, we find that C is the coefficient of z^E in

$$[\phi(z)]^a [\psi(z)]^b \dots$$

and $C \bar{E}_a$ is the coefficient of z^E in

$$\left\{ z \frac{d}{dz} [\phi(z)]^a \right\} [\psi(z)]^b \dots$$

i.e., in

$$\left\{ az \frac{d}{dz} \log \phi(z) \right\} [\phi(z)]^a [\psi(z)]^b \dots$$

These are converted into contour integrals, and we have

$$C = \frac{1}{2\pi i} \int \frac{[\phi(z)]^a [\psi(z)]^b \dots}{z^{E+1}} dz$$

$$C \bar{E}_a = \frac{1}{2\pi i} \int \frac{\left\{ az \frac{d}{dz} \log \phi(z) \right\} [\phi(z)]^a [\psi(z)]^b \dots}{z^{E+1}} dz$$

We determine the radius ϑ of the special circle of integration by finding the condition for the minimum of the integrand in C , i.e., by solving

$$\frac{d}{dz} \frac{[\phi(z)]^a [\psi(z)]^b \dots}{z^{E+1}} = 0$$

or

$$a \frac{\phi'(z)}{\phi(z)} + b \frac{\psi'(z)}{\psi(z)} + \dots - (E+1) \frac{1}{z} = 0$$

i.e., ϑ practically satisfies

$$E = a \vartheta \frac{d}{d\vartheta} \log \phi(\vartheta) + b \vartheta \frac{d}{d\vartheta} \log \psi(\vartheta) + \dots \quad (\text{IV. 14}).$$

On putting this value of ϑ into the contour integrals above, we again find that approximately

$$C = A \frac{[\phi(\vartheta)]^a [\psi(\vartheta)]^b \dots}{\vartheta^{E+1}}$$

and

(IV. 15)

$$C \bar{E}_a = A \frac{\left\{ a \vartheta \frac{d}{d\vartheta} \log \phi(\vartheta) \right\} [\phi(\vartheta)]^a [\psi(\vartheta)]^b \dots}{\vartheta^{E+1}}$$

so that

$$\begin{aligned}\overline{E}_a &= a \vartheta \frac{d}{d\vartheta} \log \phi(\vartheta) \\ \overline{E}_b &= b \vartheta \frac{d}{d\vartheta} \log \psi(\vartheta),\end{aligned}\tag{IV. 16}$$

etc.

In applying this method to a system containing free molecules where quantum states do not strictly enter, we can consider the various states defined as usual by elementary cells of the phase-diagram $\delta x \delta y \delta z \delta \xi \delta \eta \delta \zeta$ * for which the energy is $(\xi^2 + \eta^2 + \zeta^2)/2m$. The partition function is then

$$\chi(z) = \frac{\delta\sigma_1}{h^3} z^{\epsilon_1} + \frac{\delta\sigma_2}{h^3} z^{\epsilon_2} + \dots$$

where $\delta\sigma$ is written shortly for the sextuple differential $\delta x \dots \delta \zeta$, and the suffixes correspond to the various cells; ϵ_r is $(\xi_r^2 + \eta_r^2 + \zeta_r^2)/2m$, and the weight of each state is defined to be $\delta\sigma/h^3$ which we have already seen to be the justifiable method for combining non-quantum parts with quantum parts of a system, on the understanding that each quantum state is given the weight unity. In the limit $\chi(z)$ is a sextuple integral, and becomes

$$\chi(z) = \frac{v}{h^3} \iiint z^{\epsilon} d\xi d\eta d\zeta,$$

where v is the volume of the vessel.

Thus suppose there are present a vibrators with partition function $\phi(z)$ and n free molecules. The parameter ϑ is, as before, determined by

$$E = a \vartheta \frac{d}{d\vartheta} \log \phi(\vartheta) + n \vartheta \frac{d}{d\vartheta} \log \chi(\vartheta),$$

and the energy in the n gas molecules is, on the average, equal to

$$n \vartheta \frac{d}{d\vartheta} \log \chi(\vartheta).$$

* *N.B.*—Do not confuse the z co-ordinate of a molecule here with the z used as the symbol for the complex variable.

Now $z^\epsilon = e^{\epsilon \log z}$

$$= \exp [-a (\xi^2 + \eta^2 + \zeta^2)]$$

where $a = -\frac{\log z}{2m} = \frac{\log (1/z)}{2m}$.

So $\chi(z) = \frac{v}{h^3} \int_{-\infty}^{+\infty} \int \exp a (\xi^2 + \eta^2 + \zeta^2) d\xi d\eta d\zeta$

$$= \frac{v}{h^3} \left(\frac{\pi}{a}\right)^{\frac{3}{2}}$$

$$= \frac{(2\pi m)^{\frac{3}{2}} v}{h^3 [\log (1/z)]^{\frac{3}{2}}}.$$

Hence the energy of the gaseous part of the system is equal to

$$n\vartheta \frac{d}{d\vartheta} \log \frac{(2\pi m)^{\frac{3}{2}} v}{h^3 [\log (1/\vartheta)]^{\frac{3}{2}}}$$

$$= -n\vartheta \frac{d}{d\vartheta} \left\{ \frac{3}{2} \log (1/\vartheta) \right\}$$

$$= \frac{3n}{2} \cdot \frac{1}{\log (1/\vartheta)}.$$

But by the usual elementary result of kinetic theory the pressure of the gas is two-thirds of its energy per unit volume, and so

$$p = \frac{n}{v} \frac{1}{\log (1/\vartheta)},$$

and since by the usual definition of temperature

$$p = \frac{n}{v} k\theta,$$

we thus arrive once more at the relation between ϑ and temperature

$$\log (1/\vartheta) = \frac{1}{k\theta} = \mu$$

or $\vartheta = e^{-\mu}.$

We can, in a similar manner, work out other mean values. Thus the mean over all complexions of the number of

molecules or vibrators of the first type in the r^{th} quantum state is obtained thus

$$\begin{aligned} C \bar{a}_r &= \Sigma a_r \frac{a!}{a_1! a_2! \dots} p_1^{a_1} p_2^{a_2} \dots \frac{b!}{b_1! b_2! \dots} q_1^{b_1} q_2^{b_2} \dots \\ &= a p_r \Sigma \frac{(a-1)!}{a_1! a_2! \dots (a_r-1)!} p_1^{a_1} p_2^{a_2} \dots p_r^{a_r-1} \dots \\ &\quad \frac{b!}{b_1! b_2! \dots} q_1^{b_1} q_2^{b_2} \dots \end{aligned}$$

where the summation in the second line satisfies the energy condition

$$a_1 \epsilon_1 + a_2 \epsilon_2 + \dots + (a_r - 1) \epsilon_r + \dots + \Sigma b_s \eta_s = E - \epsilon_r$$

It follows that

$$\begin{aligned} C \bar{a}_r &= a p_r \int \frac{[\phi(z)]^{a-1} [\psi(z)]^b \dots dz}{z^{E-\epsilon_r+1}} \\ &\doteq a p_r A \frac{[\phi(\vartheta)]^{a-1} [\psi(\vartheta)]^b}{\vartheta^{E-\epsilon_r+1}}. \end{aligned}$$

From the value of C in (IV. 15) we find that

$$\bar{a}_r = a p_r \frac{\vartheta^{\epsilon_r}}{\phi(\vartheta)}.$$

Thus \bar{a}_r is proportional to ϑ^{ϵ_r} or, $e^{-\mu \epsilon_r}$, and we have the usual Planck partition law, degenerating to the Maxwell law for gas molecules following the classical laws.

Another important mean value is the mean of the squared energy, $\overline{E_a^2}$. Reviewing the argument by which we obtained $\overline{E_a}$, the reader will see that we shall obtain $\overline{E_a^2}$ if we employ the operator $\left(z \frac{d}{dz}\right)^2$ instead of $z \frac{d}{dz}$. Thus $C \overline{E_a^2}$ is the coefficient of z^E in the expansion of

$$\left\{ \left(z \frac{d}{dz} \right)^2 [\phi(z)]^a \right\} [\psi(z)]^b \dots$$

and therefore, is equal to

$$\frac{1}{2\pi i} \int \frac{\left\{ \left(z \frac{d}{dz} \right)^2 [\phi(z)]^a \right\} [\psi(z)]^b \dots}{z^{E+1}} dz.$$

which is approximately equal to

$$\frac{A \left\{ \left(\vartheta \frac{d}{d\vartheta} \right)^2 [\phi(\vartheta)]^a \right\} [\psi(\vartheta)]^b \dots}{\vartheta^{E+1}}$$

Hence, using the value of C in (IV . 15) we have

$$\begin{aligned} \overline{E_a^2} &= \frac{\left(\vartheta \frac{d}{d\vartheta} \right)^2 [\phi(\vartheta)]^a}{[\phi(\vartheta)]^a} \\ &= \frac{\vartheta \frac{d}{d\vartheta} \left\{ \vartheta \frac{d}{d\vartheta} [\phi(\vartheta)]^a \right\}}{[\phi(\vartheta)]^a} \\ &= \frac{\vartheta \frac{d}{d\vartheta} \left\{ a\vartheta [\phi(\vartheta)]^{a-1} \phi'(\vartheta) \right\}}{[\phi(\vartheta)]^a} \\ &= \frac{\vartheta \frac{d}{d\vartheta} \left\{ \left[a\vartheta \frac{d}{d\vartheta} \log \phi(\vartheta) \right] [\phi(\vartheta)]^a \right\}}{[\phi(\vartheta)]^a} \\ &= \frac{\vartheta \frac{d}{d\vartheta} \left\{ \overline{E_a} [\phi(\vartheta)]^a \right\}}{[\phi(\vartheta)]^a} \quad \text{by (IV . 16)} \\ &= \vartheta \frac{d\overline{E_a}}{d\vartheta} + \overline{E_a} \cdot \frac{a\vartheta \phi'(\vartheta) [\phi(\vartheta)]^{a-1}}{[\phi(\vartheta)]^a} \\ &= \vartheta \frac{d\overline{E_a}}{d\vartheta} + (\overline{E_a})^2. \end{aligned}$$

The fluctuation of the energy is measured by the mean value of the square of the difference $E_a - \overline{E_a}$. Now

$$(E_a - \overline{E_a})^2 = E_a^2 - 2 E_a \overline{E_a} + (\overline{E_a})^2$$

and the mean value of this is equal to

$$\begin{aligned} &\overline{E_a^2} - 2 \overline{E_a} \overline{E_a} + (\overline{E_a})^2 \\ &= \overline{E_a^2} - (\overline{E_a})^2 \\ &= \vartheta \frac{d\overline{E_a}}{d\vartheta} \end{aligned}$$

$$\begin{aligned}
&= e^\mu \frac{d\bar{E}_a}{d\mu} \frac{d\mu}{d\theta} \\
&= e^\mu \frac{d\bar{E}_a}{d\mu} \frac{1}{e^\mu} \\
&= \frac{d\bar{E}_a}{d\theta} \frac{d\theta}{d\mu} \\
&= k\theta^2 \frac{d\bar{E}_a}{d\theta},
\end{aligned}$$

a result which Einstein made use of in treating fluctuations of radiation in a temperature enclosure in the early days of quantum theory. The legitimate use of the approximation in the case of the operator $(z d/dz)^2$ requires careful analysis, but it appears that it is quite rigorous in a temperature bath.

In the *Proc. Roy. Soc.*, A 113, p. 432 (1926), will be found a paper by Fowler reviewing recent statistical theory, and showing how the method of partition functions can be applied to the statistics of Einstein and Bose, and that of Fermi and Dirac.

APPENDIX ON COLLISION-FORMULÆ AND CHEMICAL KINETICS

IN the treatment of systems in statistical equilibrium it is postulated that energy can be transferred from molecule to molecule, but no assumptions concerning the mechanism by which energy is so transferred are required. When, however, we deal with systems which are not in equilibrium, it is only natural to expect that we shall have to take more careful account of the nature of the forces which act between molecules; for while the ultimate state of equilibrium attained is independent of the special laws of the intermolecular forces, the manner in which that state is approached and the rate of transformation is clearly dependent on them.

The problems raised by such considerations hardly come within the scope of a book which is an "Introduction," and which has already grown to the limits set by the capacities and needs of its probable readers. However, it may be of some value if a further appendix, which will not seriously encroach on the student's time and patience, is added, and one or two matters which are fundamental in the treatment of non-equilibrium states are dealt with. They concern the frequency of molecular encounters and the bearing which this has on chemical kinetics.

I. *Collisions between Molecules in a Gas.*—In the Kinetic Theory of Gases a very simple type of intermolecular action is assumed for many purposes. An encounter (that is the interval during which two molecules are within the sphere of one another's action) is considered to be so brief in relation to the time of free path that it is pictured as a "collision" which takes place instantaneously when the centres of the two molecules are separated by a definite distance which we denote by σ . In short, the molecules are visualised as "hard spheres," σ being equal to the

diameter if they are like molecules and to the sum of their radii if they are unlike.

For the reader's guidance through this section, which involves some rather tedious steps, it may be as well at the outset to give him a preliminary summary to the various formulæ obtained in it.

(I. 1) is a general result for the number of collisions per unit time between two types of molecules in a gas mixture whose velocities are confined to narrow ranges of velocity.

(I. 2) is the specialised form of (I. 1) when the mixture is in statistical equilibrium.

(I. 3) is the total number of collisions per unit time in the mixture when in equilibrium.

(I. 4) and (I. 5) are formulæ for the total number of collisions in a gas consisting of one type of molecule.

(I. 6) is a value for the mean free path of a molecule in a gas.

(I. 7) and (I. 8) refer to the collisions which involve a *relative* velocity between colliding molecules which lies within narrow limits or is greater than an assigned value.

(I. 9) and (I. 10) are similar formulæ which involve the relative velocity *of approach*, *i.e.*, the component of relative velocity along the line of centres of the colliding molecules.

The last four formulæ are of considerable value in the problem of chemical reaction in gases.

In treating the problem of collision-frequency we consider an enclosure in which there are present N_1 molecules of one type per unit volume and N_2 of a second type also per unit volume. We introduce a velocity diagram partitioned as usual into cells; at a given instant let the number of representative points of molecules the first type in the r th cell be $\nu_{1r} \delta\omega_r$, where $\delta\omega_r$ is written for $\delta u_r \delta v_r \delta w_r$ (u_r, v_r, w_r are the components of the velocity corresponding to the central point of the cell). The number of the second type is $\nu_{2r} \delta\omega_r$. We are not considering at the moment an equilibrium distribution, but there is some law of distribution, and so ν_{1r} will be some function of u_r, v_r, w_r . Represent it by $f_1(u_r, v_r, w_r, t)$; the time-variable must, of course, be involved if the distribution is non-equilibrium. Similarly,

ν_{2r} is equal to $f_2(u_r, v_r, w_r, t)$, f_1 and f_2 not being of necessity the same functional form. If the distribution should be one of statistical equilibrium the function $f_1(u, v, w, t)$ would be the Maxwell function

$$N_1 \left(\frac{\mu m_1}{2\pi} \right)^{\frac{3}{2}} \exp \left[-\frac{1}{2} \mu m_1 (u^2 + v^2 + w^2) \right]$$

and $f_2(u, v, w, t)$ would be

$$N_2 \left(\frac{\mu m_2}{2\pi} \right)^{\frac{3}{2}} \exp \left[-\frac{1}{2} \mu m_2 (u^2 + v^2 + w^2) \right]$$

(See expression (4.1.1) and equation (4.1.8), remembering that $\xi = mu$, etc.) Our first problem is to obtain the probable number of collisions per unit time between the molecules of the first type and those of the second.

First of all let us analyse the relative situation of two molecules, with their representative points in the a th and in the b th velocity-cells respectively, which will lead to a collision within an interval δt . Let the reader be careful to guard against confusing situations of representative points in velocity-cells with situations of the points by which we sometimes idealise the molecules themselves in the enclosure. The two cells might be very far apart indeed in the velocity-diagram without necessarily implying the impossibility of a collision within a very brief time of many of the molecules represented. It will be realised after little thought that one important factor in settling the possibility of a collision within an interval δt between two assigned molecules is the *relative* velocity $u_b - u_a, v_b - v_a, w_b - w_a$; another is the angle between the direction of this relative velocity and the direction of the line of centres of the two molecules from the centre of the b molecule to the centre of the a molecule. If this angle is denoted by θ , and if σ represents the sum of the radii of the two molecules, there will be a collision within the interval δt if the centres of the molecules are now separated by a distance which lies between σ and $\sigma + r \cos \theta \delta t$, where r is the magnitude of the relative velocity and is equal to $\{(u_b - u_a)^2 + (v_b - v_a)^2 + (w_b - w_a)^2\}^{\frac{1}{2}}$. (The angle θ is necessarily less than a right angle.) Thus the centre of any molecule of the group b which would collide within time δt

with a specified molecule of group a , the "line of centres angle" being between θ and $\theta + \delta\theta$, would have to lie in a ring-shaped space whose circumference is $2 \pi \sigma \sin \theta$, and whose section is an elementary rectangle with sides $\sigma \delta\theta$ and $r \cos \theta \delta t$. The volume of this ring is $2 \pi \sigma^2 r \sin \theta \cos \theta \delta\theta \delta t$. Let us assume that δt is chosen to have such a value that this ring contains on the average one molecule of the group b , so that it is therefore equal to $(\nu_{2b} \delta\omega_b)^{-1}$ in volume; then δt must be equal to

$$\frac{1}{\nu_{2b} \delta\omega_b 2 \pi \sigma^2 r \sin \theta \cos \theta \delta\theta}$$

and in this time there is on the average one collision between a specified molecule of the group a and any molecule of the group b having the defined line-of-centres relation. So in one second there are

$$\nu_{2b} \delta\omega_b 2 \pi \sigma^2 r \sin \theta \cos \theta \delta\theta$$

collisions between a specified molecule of the group a and any molecule of the group b having the defined line-of-centres relation. Integrating with respect to θ between the limits $\theta = 0$ and $\theta = \pi/2$, we obtain the number of collisions per second between a specified molecule of the group a and any molecule of the group b . The result is

$$\nu_{2b} \delta\omega_b \pi \sigma^2 r.$$

As there are $\nu_{1a} \delta\omega_a$ of the first type molecules in the a th phase-cell, the number of collisions per unit volume per unit time between molecules of the first type in the velocity-condition represented by the a th velocity cell and molecules of the second type in the velocity-condition represented by the b th phase-cell is

$$\pi \sigma^2 \nu_{1a} \nu_{2b} r \delta\omega_a \delta\omega_b$$

that is,

$$\pi \sigma^2 f_1(u_a, v_a, w_a) f_2(u_b, v_b, w_b) r \quad \cdot \quad \cdot \quad \cdot \quad (I. 1) \\ du_a dv_a dw_a du_b dv_b dw_b$$

The total number of collisions per unit volume per second between all the molecules of type 1 and all those of type 2 will be given by the integral of the expression (I. 1) between the limits plus and minus infinity for the six velocity com-

ponents. Of course, such an integration could in general be carried out only by rather laborious methods of approximation. When the gas mixture is in equilibrium and we can use the Maxwell law of distribution, the integration can be effected by means of the table of integrals on p. 17, though not quite so directly or simply as might appear at the first glance. The trouble arises owing to the appearance of the factor r , *i.e.*, $\{(u_b - u_a)^2 + \dots\}^{\frac{1}{2}}$ in (I. 1), but the difficulty can be surmounted by a transformation of variables and, in order to explain this point, we shall have to digress for a moment and introduce the reader to two necessary lemmas.

The first is very simple. Let α, β, γ represent the components of the velocity of the centre of mass of two particles m_1 and m_2 , and let ξ, η, ζ stand for the components of the relative velocity r , so that

$$\alpha = \frac{m_1 u_a + m_2 u_b}{m_1 + m_2}$$

etc.,

and

$$\xi = u_b - u_a$$

etc.

It is then easy to show that the combined kinetic energy of the two particles which is

$$\frac{1}{2} m_1 (u_a^2 + v_a^2 + w_a^2) + \frac{1}{2} m_2 (u_b^2 + v_b^2 + w_b^2)$$

is equal to

$$\begin{aligned} \frac{1}{2} (m_1 + m_2) (\alpha^2 + \beta^2 + \gamma^2) + \frac{1}{2} m_{12} (\xi^2 + \eta^2 + \zeta^2) \\ = \frac{1}{2} (m_1 + m_2) c^2 + \frac{1}{2} m_{12} r^2 \end{aligned}$$

where c is the velocity of the centre of mass and $m_{12} = m_1 m_2 / (m_1 + m_2)$. This result enables us to write

$$f_1(u_a, v_a, w_a) f_2(u_b, v_b, w_b) r$$

which appears as part of (I. 1) in the form

$$N_1 N_2 \left(\frac{\mu^2 m_1 m_2}{4 \pi^2} \right)^{\frac{3}{2}} \exp. \left[-\frac{1}{2} \mu \{ (m_1 + m_2) c^2 + m_{12} r^2 \} \right] r$$

when we are considering the equilibrium distribution.

The second theorem is concerned with substituting for

the sextuple differential $du_a \dots dw_b$ in (I. 1) an expression involving the sextuple differential $d\alpha d\beta d\gamma d\xi d\eta d\zeta$. Consider for the moment a plane diagram and a point A on it which moves over a certain extension in the plane. Let x, y stand for the current co-ordinates of A, and let us consider another point B whose co-ordinates (X, Y) are connected with those of A by the relations

$$\begin{aligned} X &= kx + ly \\ Y &= \kappa x + \lambda y \end{aligned}$$

where k, l, κ, λ , are any constants. The point B will move over a second extension in the plane as A moves over the first. It can be proved that the area of the second extension bears to that of the first the ratio $k\lambda - \kappa l$. This is most readily seen by noting that if A' and A'' are two positions of A, and B' and B'' are the corresponding positions of B, then the area of the triangle OB'B'' is equal to

$$\begin{aligned} & \frac{1}{2} (X' Y'' - X'' Y') \\ &= \frac{1}{2} \{ (kx' + ly') (\kappa x'' + \lambda y'') - (kx'' + ly'') (\kappa x' + \lambda y') \} \\ &= \frac{1}{2} (k\lambda - \kappa l) (x'y'' - x''y') \\ &= (k\lambda - \kappa l) \times \text{area of the triangle OA'A''}. \end{aligned}$$

The result stated above follows when one recalls that any enclosed area can be divided into elementary triangles having a common vertex within the area.

If we now consider a two-dimensional diagram in which we represent u_a and u_b by a point A, and α and ξ by a point B, it follows that an extension in the diagram embracing a continuum of values of u_a and u_b and the extension embracing the corresponding values of α and ξ are equal in area, since in this case

$$\begin{aligned} k &= \frac{m_1}{m_1 + m_2}, \quad l = \frac{m_2}{m_1 + m_2} \\ \kappa &= -1, \quad \lambda = +1 \end{aligned}$$

As this applies to elementary extensions just as much as to finite, we can replace $du_a du_b$ by $d\alpha d\xi$ in an integral. A similar result holds for the other components.

After this digression we can return to the general expres-

sion (I. 1), and, in the case of the state of equilibrium, write it as

$$\pi \sigma^2 N_1 N_2 \left(\frac{\mu^2 m_1 m_2}{4 \pi^2} \right)^{\frac{3}{2}} \exp. \left[-\frac{1}{2} \mu \{ (m_1 + m_2) c^2 + m_{12} r^2 \} \right] r \, d\alpha \, d\beta \, d\gamma \, d\xi \, d\eta \, d\zeta \quad . \quad . \quad . \quad (I. 2)$$

The integral of this over all possible values of $\alpha, \beta, \gamma, \xi, \eta, \zeta$, can be separated into two triple integrals, which, apart from the initial factors, are

$$\iiint \exp \left[-\frac{1}{2} \mu (m_1 + m_2) c^2 \right] d\alpha \, d\beta \, d\gamma$$

and

$$\iiint \exp \left[-\frac{1}{2} \mu m_{12} r^2 \right] r \, d\xi \, d\eta \, d\zeta.$$

By a familiar transformation the first becomes

$$4 \pi \int_0^\infty \exp \left[-\frac{1}{2} \mu (m_1 + m_2) c^2 \right] c^2 dc$$

the second

$$4 \pi \int_0^\infty \exp \left[-\frac{1}{2} \mu m_{12} r^2 \right] r^3 dr$$

The first of these has the value

$$4 \pi \cdot \frac{\pi^{\frac{1}{2}}}{4} \left(\frac{2}{\mu (m_1 + m_2)} \right)^{\frac{3}{2}}$$

(See the table of integrals on p. 17, No. 2.)

The second has the value

$$4 \pi \frac{1}{2} \left(\frac{2}{\mu m_{12}} \right)^2$$

(See the table, No. 3.)

Thus the expression (I. 2), when integrated, becomes

$$\pi \sigma^2 N_1 N_2 \left(\frac{\mu^2 m_1 m_2}{4 \pi^2} \right)^{\frac{3}{2}} \left(\frac{2 \pi}{\mu (m_1 + m_2)} \right)^{\frac{3}{2}} \frac{8 \pi}{\mu^2 m_{12}^2}$$

which simplifies to

$$2 \sigma^2 N_1 N_2 \left(\frac{2 \pi}{\mu m_{12}} \right)^{\frac{1}{2}} \quad . \quad . \quad . \quad (I. 3)$$

where we recall that $\mu = (k\theta)^{-1}$, $m_{12} = m_1 m_2 / (m_1 + m_2)$, and σ is the sum of the radii of the two molecules. This expression (I. 3) is the total number of collisions per unit volume per unit time between molecules of the first kind

and molecules of the second kind in a gas mixture which is in a state of equilibrium.

We can easily obtain from this the number of collisions in a simple gas whose concentration is N molecules per unit volume. The formula (I. 3) will give it if we put N_1 equal to N_2 , m_1 equal to m_2 , and divide by 2; for, as it stands, (I. 3) would count each collision twice. Thus the collision-frequency in unit volume of the gas is

$$\sigma^2 N^2 \left(\frac{4 \pi}{\mu m} \right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (I. 4)$$

$$\text{or} \quad \sigma^2 N^2 \left(\frac{4 \pi k \theta}{m} \right)^{\frac{1}{2}}$$

$$\text{i.e.,} \quad \sigma^2 N^2 \left(\frac{4 \pi R \theta}{M} \right)^{\frac{1}{2}}$$

where M is the gram-molecular mass, and R the gram-molecular gas constant.

This can be thrown into another very useful form. At the end of Chapter IV., we calculated the mean value of squared velocities of the molecules in a gas in the equilibrium state. We can just as easily calculate the mean velocity. If we now use the symbol c to represent the velocity of a molecule the number per unit volume whose velocities lie between c and $c + \delta c$ is

$$4 \pi N \left(\frac{\mu m}{2 \pi} \right)^{\frac{3}{2}} \exp \left(- \frac{1}{2} \mu m c^2 \right) c^2 \delta c.$$

Hence the average velocity is

$$4 \pi \left(\frac{\mu m}{2 \pi} \right)^{\frac{3}{2}} \int_0^{\infty} \exp \left(- \frac{1}{2} \mu m c^2 \right) c^3 \delta c$$

which, by using the third integral in the table on p. 17, is equal to

$$\begin{aligned} & 4 \pi \left(\frac{\mu m}{2 \pi} \right)^{\frac{3}{2}} \cdot \left(\frac{2}{\mu m} \right)^{\frac{1}{2}} \cdot \frac{1}{2} \\ &= \frac{4}{(2 \pi \mu m)^{\frac{1}{2}}} \end{aligned}$$

Hence the expression (I. 4) for the collision-frequency in unit volume is equal to

$$\frac{\pi}{\sqrt{2}} \sigma^2 N^2 \bar{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (I. 5)$$

where \bar{c} is the average molecular velocity.

Since each collision terminates two free paths there are $\sqrt{2} \pi \sigma^2 N^2 \bar{c}$ free paths described in unit time by the N molecules. This gives for the average interval of time between collisions the value

$$\frac{1}{\sqrt{2} \pi \sigma^2 N^2 \bar{c}}$$

and if we multiply this by \bar{c} we have an estimate for the average length of a free path ; it is

$$\frac{1}{\sqrt{2} \pi \sigma^2 N^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (I. 6)$$

There are other methods of calculating mean free path, but they all give values approximately to

$$\frac{.7}{\pi \sigma^2 N^2}$$

Returning to the expression (I. 2) and only integrating with respect to α, β, γ , we can obtain the number of collisions between molecules of type 1 and molecules of type 2 in a mixture whose *relative* velocity lies between limits r and $r + \delta r$; it is

$$\begin{aligned} & \pi \sigma^2 N_1 N_2 \left(\frac{\mu^2 m_1 m_2}{4 \pi^2} \right)^{\frac{3}{2}} 4 \pi \frac{\pi^{\frac{1}{2}}}{4} \left(\frac{2}{\mu(m_1 + m_2)} \right)^{\frac{3}{2}} \\ & \times 4 \pi \exp \left[-\frac{1}{2} \mu m_{12} r^2 \right] r^3 \delta r \end{aligned}$$

that is

$$\sigma^2 N_1 N_2 (2 \pi \mu^3 m_{12}^3)^{\frac{1}{2}} \exp \left[-\frac{1}{2} \mu m_{12} r^2 \right] r^3 \delta r \quad . \quad . \quad (I. 7)$$

a formula of considerable value in connection with the problem of chemical reaction in gases.

If (I. 7) is integrated for all values of r from a definite value from r_0 to ∞ , we find the number of collisions in which the relative velocity is greater than r_0 . Now

$$\int_{r_0}^{\infty} e^{-\alpha r^2} r^3 dr \\ = \frac{1}{2} \int_{y_0}^{\infty} e^{-\alpha y} y dy$$

(where y is written for r^2)

$$= \frac{1}{2\alpha} \left\{ \int_{y_0}^{\infty} e^{-\alpha y} dy - \int_{y_0}^{\infty} d(e^{-\alpha y} y) \right\}$$

(integrating by parts)

$$= \frac{1}{2\alpha} \left[-\frac{e^{-\alpha y}}{\alpha} - e^{-\alpha y} y \right]_{y_0}^{\infty} \\ = \frac{1}{2\alpha} \left(\frac{1}{\alpha} + y_0 \right) e^{-\alpha y_0} \\ = \frac{1 + \alpha r_0^2}{2\alpha^2} e^{-\alpha r_0^2}$$

Hence the number of collisions in which the relative velocity is greater than r_0 works out to be

$$\frac{\sigma^2 N_1 N_2 (2\pi\mu^3 m_{12}^3)^{\frac{1}{2}}}{\frac{1}{2}\mu^2 m_{12}^2} \left(1 + \frac{\mu m_{12} r_0^2}{2} \right) \exp \left[-\frac{1}{2}\mu m_{12} r_0^2 \right]$$

which by (I. 3) is equal to

$$C \left(1 + \frac{\mu m_{12} r_0^2}{2} \right) \exp \left[-\frac{1}{2}\mu m_{12} r_0^2 \right] \quad \text{(I. 8)}$$

where C stands for the total number of collisions per unit time.

It is also of interest in connection with chemical kinetics to obtain the number of collisions in which the relative velocity of approach of the colliding molecules, *i.e.*, the component of r parallel to the line of centres, is within a narrow range of values. To do so we revert to the considerations leading to (I. 1) and (I. 2) and observe, that had we not integrated with respect to θ at an early stage, we would have found that the number of collisions between molecules with relative velocities between r and $r + \delta r$ and line-of-centres angle between θ and $\theta + \delta\theta$ would be given by multiplying (I. 7) by $2 \sin \theta \cos \theta \delta\theta$, *i.e.*, it would be

$$2\sigma^2 N_1 N_2 (2\pi\mu^3 m_{12}^3)^{\frac{1}{2}} \exp \left[-\frac{1}{2}\mu m_{12} r^2 \right] r^3 \sin \theta \cos \theta \delta r \delta \theta$$

In such collisions the component of relative velocity parallel to the line of centres is practically $r \cos \theta$; denote it by s . If this has to be greater than s_0 , then r must certainly be greater than s_0 , and, for a given value of r , $\cos \theta$ must lie between unity and s_0/r . So we must integrate the expression just written first with respect to θ between the limits $\theta = 0$ and $\theta = \cos^{-1}(s_0/r)$, and then with respect to r from s_0 to infinity. By methods similar to that used for obtaining (I. 8) we find the result to be

$$C \exp [-\mu m_{12} s_0^2] \quad . \quad . \quad . \quad . \quad (I. 9)$$

If the component of relative velocity is to lie within a narrow range of values s to $s + \delta s$, the number is given as a differential of (I. 9); it is

$$2 \mu m_{12} C \exp [-\mu m_{12} s^2] s \delta s \quad . \quad . \quad . \quad (I. 10)$$

II. *Collision-Frequency and Equilibrium. The H Theorem.*—The formula (I. 1) is quite general, and in deriving (I. 2) we assumed the Maxwell form for the function $f(u, v, w)$. As a matter of fact, the Maxwell distribution law for a gas in equilibrium can be deduced from (I. 1), and, indeed, such methods of deduction were the first to be employed before the work of Boltzmann, Gibbs and Jeans had revealed their inherent weakness, and in doing so developed the methods of Statistical Mechanics which are “rigorous” in the true meaning of that word; viz., deduced with a clear perception of the assumptions which we are making in the proof. A few words about this matter will not be out of place.

Considering the expression (I. 1) for a gas with one type of molecule, viz.,

$$\pi \sigma^2 f(u_a, v_a, w_a) f(u_b, v_b, w_b) r d\omega_a d\omega_b,$$

we see that if it were integrated for all values of u_b, v_b, w_b , between plus and minus infinity, the result would be the rate at which molecules whose representative points are in the a th velocity-cell are leaving that velocity-state owing to encounters. It is theoretically possible, if we know enough about the molecules, to determine also the rate at which molecules are entering that velocity-state from other states. For that purpose it is essential to know sufficient

facts about the law of the forces between the molecules. As before, the simplest assumption is that of an instantaneous collision, combined also with the further assumption of perfect elasticity which implies that no energy of translation is converted into internal energy, *i.e.*, that the spheres are "hard and structureless."

There is no space to go into details of the proof (the reader will find them in full in Jeans' *Dynamical Theory of Gases*, Chapter II.). They show how one can find by dynamical methods the equations which give $u_c, v_c, w_c, u_d, v_d, w_d$ and ϕ in terms of $u_a, v_a, w_a, u_b, v_b, w_b$ and θ , such that a collision between a molecule in the c th velocity-cell and one in the d th cell with a line-of-centres angle between ϕ and $\phi + \delta\phi$ will result in one molecule entering the velocity-state a and the other the velocity-state b , the line-of-centres angle lying between θ and $\theta + \delta\theta$ (with the molecules, of course, separating and not approaching). The number of such collisions, is, of course,

$$2\pi \sigma^2 f(u_c, v_c, w_c) f(u_d, v_d, w_d) r' \sin \phi \cos \phi \delta\phi \delta\omega_c \delta\omega_d$$

where r' is the relative velocity of molecules of the class c to those of the class d . Concerning this expression there are two important remarks. First of all, owing to the equations referred to above, $f(u_c, v_c, w_c) f(u_d, v_d, w_d)$ can be expressed as a function of $u_a, v_a, w_a, u_b, v_b, w_b$ and θ . Secondly, *by an application of the Liouville Theorem*, it can be shown that the differential expression $r' \sin \phi \cos \phi \delta\phi \delta\omega_c \delta\omega_d$ can be replaced by $r \sin \theta \cos \theta \delta\theta \delta\omega_a \delta\omega_b$. It therefore follows that the net rate at which molecules in the velocity-state a are gaining in number at the expense of other states is obtained by integrating the following expression for all values of u_b, v_b, w_b , between plus and minus infinity and for values of θ from 0 to $\pi/2$ —

$$\left\{ f(u_c, v_c, w_c) f(u_d, v_d, w_d) - f(u_a, v_a, w_a) f(u_b, v_b, w_b) \right\} \\ 2\pi \sigma^2 \delta\omega_a r \sin \theta \cos \theta d\omega_b d\theta \quad . \quad . \quad . \quad (II. 1)$$

Now if the state is one of equilibrium this integral must be zero, and one very obvious method of effecting that is to make the expression within the $\{ \}$ brackets equal to

zero. Proceeding on that line for the moment, it follows that

$$\begin{aligned} & \log f(u_a, v_a, w_a) + \log f(u_b, v_b, w_b) \\ &= \log f(u_c, v_c, w_c) + \log f(u_d, v_d, w_d). \end{aligned}$$

It then appears that the only way to satisfy this functional equation consistent with the dynamical relations which connect u_a, \dots, w_b with u_c, \dots, w_d , is to write the function $f(u, v, w)$ equal to

$$A \exp [-\mu \{ (u - u_o)^2 + (v - v_o)^2 + (w - w_o)^2 \}],$$

where A, μ, u_o, v_o, w_o are constants. This is essentially a Maxwell distribution for velocities $u - u_o, v - v_o, w - w_o$, which simply means that it refers to a gas in statistical equilibrium whose centre of gravity is moving with a uniform velocity u_o, v_o, w_o , in our frame of reference.

Now from our earlier investigations we know that we were bound to reach this conclusion for equilibrium with any mechanism which obeys dynamical laws, let alone the very simple one we have postulated. Nevertheless, without this general support for the argument, one must admit one weakness in it. We have, for equilibrium, to equate the integral of (II. 1) to zero, and we adopted one very obvious way of doing this, but it is by no means obvious that it is the *only way*. It is on general grounds quite possible that functional forms of $f(u, v, w)$ might exist which without making the integrand zero for all corresponding values of the variables would, nevertheless, make the integral of it over the whole range of those variables vanish. In that case equilibrium would be preserved without the "detailed balancing," as it is called, which would prevail if we make the more simple assumption referred to. A great deal of discussion on this matter took place during the last years of the nineteenth century. At length Boltzmann propounded a famous theorem, called the H theorem, which ostensibly settled the matter by showing that for elastic collisions, at all events, detailed balancing was the only method of preserving the gas in its equilibrium state. Yet it was pointed out in the discussion that Boltzmann's Theorem apparently was in flat contradiction with the reversibility

inherent in dynamical occurrences. In the clearing up of this point and in the strict determination of the sense in which Boltzmann's Theorem is true, one may say that Statistical Mechanics was born and methods for the treatment of molecular phenomena without resort to any dynamical details of intermolecular collisions developed.

Boltzmann, in his proof of the H theorem began by constructing the function

$$\iiint f(u, v, w) \log f(u, v, w) du dv dw \quad . \quad . \quad . \quad (II. 2)$$

the integral extending over all values of the velocity components between plus and minus infinity. This is really a function of t ; for the reader will remember that in cases of non-equilibrium the time-variable should really be included among the variables. Boltzmann denoted it by the symbol H . If we differentiate the expression with regard to the time, we find that

$$\frac{dH}{dt} = \iiint (1 + \log f) \frac{\partial f}{\partial t} du dv dw.$$

The value of $\partial f / \partial t$ for a particular value of u, v, w , can be derived from (II. 1) in the manner indicated above, *elastic collisions being postulated*. The details can once more be found in Jeans' book. The upshot is to prove that dH/dt can only be zero or negative, and that if it is zero, then *necessarily*

$$f(u_a, v_a, w_a) f(u_b, v_b, w_b) = f(u_c, v_c, w_c) f(u_d, v_d, w_d) \quad (II. 2)$$

Now H depends solely on the law of distribution of the velocities at the moment and so remains unchanged if the law of distribution remains unchanged. Thus, if there is equilibrium it follows that dH/dt must be zero, and it equally follows that (II. 2) must be true, and detailed balancing with Maxwell's law is deduced as necessary for equilibrium. This is satisfactory so far as it goes, but the further part of the theorem; viz., that if dH/dt is not zero, it must be negative, which appears to be logically bound up with the other part, gives us pause. If it is true, then the most

obvious interpretation is that if the state is not an equilibrium one, the function H will continually decrease until it reaches a minimum value and retain this value thereafter, the system having in the meantime attained equilibrium. Now this is inconsistent with the dynamical principles from which it has been presumably deduced, for by these principles any motion is reversible ; so if a certain state of motion is possible for the system, that state is also possible in which the position of each molecule at any moment is unchanged and its velocity exactly reversed in direction. But after such reversal, the system, *assumed to consist of perfectly elastic spherical molecules*, would exactly retrace the " path " by which it reached this state in the original motion. If in that motion H was decreasing, then obviously in this reversed motion H will increase, and so to every state of motion in which H decreases there corresponds another in which it increases. The solution of this paradox is revealed when attention is drawn to the fact that in the previous section the various formulæ are values for the *probable* number of collisions per unit time ; the predicted behaviour of the H function is not given with absolute certainty ; only its most probable but not perfectly certain behaviour is given by the result. Presumably, if the gas is not in a state of equilibrium, H will in all likelihood decrease ultimately to its minimum equilibrium value, but it is not guaranteed that it may not in the meantime fluctuate now and then to higher values than that possessed at the moment. In fact, the reader will " see the light " when he recalls the standpoint of Statistical Mechanics as he has learnt it in the text, especially in Chapters XXIII. and XXIV. We can make no definite prediction about the behaviour of the system in any given state ; the conditions are too complex to work out in detail. We can say with some assurance what is its most likely behaviour, our ideas of probability being based on the general behaviour of an *ensemble* of similar systems. Indeed, we have in effect met the H function quite early in the book. If, instead of using the integral notation of (II. 2), we revert to our original notation in connection with the partition of a velocity-diagram into c cells, then for a distribution in

which there are n_1 representative points in the first cell, n_2 in the second, etc., the H function is essentially

$$\sum_{r=1}^c n_r \log n_r,$$

apart from a constant term involving the size of the cell. Thus H is just

$$n \log n - W(n_1, n_2, \dots, n_c)$$

and the conclusions drawn previously concerning the probable but not certain increase of the W function to a maximum value are just as true in this strictly limited sense concerning the behaviour of the H function. It was, as we have stated, in this clarification of the H theorem that the true standpoint of Statistical Mechanics, freed, as far as equilibrium conditions are concerned, from all connection with special collisional mechanisms, stood revealed.

III. *The Kinetics of Gas Reactions in a Homogeneous System.*—If in a mixture of two gases a reaction takes place in which the two dissimilar molecules unite to form a new molecule or exchange parts to yield two different molecules, it is clear that the process is dependent on collisions in some way. If, however, a reaction occurs in a simple gas in which the original molecules decompose into two or more molecules, it is not so obvious that collisions necessarily play any part in the process.

Taking the first case, there is very clear evidence that the rate of the reaction, where this is slow enough to be measured, is not simply dependent on the collision-frequency, *i.e.*, simply proportional to it. Of course, there does not exist a state of equilibrium if a chemical reaction is going on; nevertheless, the formulæ of Section I. for the equilibrium state will apply approximately if the rate is slow enough, and if the rate were proportional to the *total* number of collisions per second between the two types of reacting molecules, then the rate would be equal to

$$\kappa C_1 C_2$$

where κ is the so-called “velocity-constant” and C_1 and C_2 are the concentrations of the molecules. Now, undoubtedly, quite a number of gas reactions occur in which the rate is

proportional to the product of the concentrations; and there exist simple gas reactions in which the rate is proportional to the square of the concentrations. Yet a glance at (I. 3) or (I. 4) will show that on such an assumption the velocity-constant would vary as θ^1 where θ is the absolute temperature at which the reaction is allowed to take place; but this is violently at variance with the facts; for in such reactions of the second order as have been carefully studied the value of κ will double or even treble for a rise of temperature comparable with 10° .

As every physical chemist knows, it was Arrhenius who was the first to offer a hypothesis to deal with this discrepancy. About 1890 he suggested that the reaction did not take place between molecules in their normal state, but between molecules in an "activated" state, *i.e.*, that the change was due to collisions between special groups of molecules, and this hypothesis fits very nicely into the "quantum scheme of things" now existing. For whatever might be the change that is produced in the structure of a molecule by "activation," it was postulated that it was effected by the acquisition of energy far above the normal amount in an average molecule, so that nowadays we simply regard an activated molecule as a molecule in a higher quantum state. For a full discussion of the idea of activation, we must refer the reader to a text of Physical Chemistry. (See, for instance, W. C. Lewis's *System of Physical Chemistry*, Vol. I., Chapter IX.; Vol. III., Chapter VII.) All that we are concerned with at the moment is to show how on statistical grounds it leads very simply to Arrhenius' well-known law of the change of velocity constant with temperature. It is quite sufficient for our purpose to assume that each molecule has, as regards internal phases, a normal or lower quantum state indicated by the suffix n , and one upper quantum state (activated) indicated by the suffix a . The result is just as easily proved for the assumption of many higher quantum states, but the mathematical expressions are more complicated to handle.

Thus, for the molecules of type 1, the number in the lower quantum state are proportional to $w_{1n} \exp(-\mu \epsilon_{1n})$ where

w_{1n} is the *à priori* probability of that state and ϵ_{1n} the internal energy. The number in the activated state is proportional to $w_{1a} \exp(-\mu \epsilon_{1a})$. (Observe that we are assuming the expressions for the equilibrium state to be sufficiently good approximations for a state of reaction; this will require some consideration later.) For the second molecule similar expressions hold. Thus the number of activated molecules of type 1, existing at the moment when there are altogether N_1 molecules of this type which have not yet gone into reaction, is

$$N_1 \frac{w_{1a} \exp(-\mu \epsilon_{1a})}{w_{1n} \exp(-\mu \epsilon_{1n}) + w_{1a} \exp(-\mu \epsilon_{1a})} \quad (\text{III. 1})$$

The activated molecules of type 2 are

$$N_2 \frac{w_{2a} \exp(-\mu \epsilon_{2a})}{w_{2n} \exp(-\mu \epsilon_{2n}) + w_{2a} \exp(-\mu \epsilon_{2a})} \quad (\text{III. 2})$$

Arrhenius' assumption is that the rate of reaction is proportional in the collision-frequency of the activated molecules. It is not necessarily assumed that all such collisions lead to a reaction; other circumstances, such as state of orientation, for example, might have to be taken into account; but it is assumed that a definite fraction of such collisions are effective. Calling this fraction f_{12} , we see that the rate of reaction taken to be the rate at which molecules pass out of the reactant condition, viz., $-dN_1/dt$ or $-dN_2/dt$, is obtained as the product of (III. 1), (III. 2), f_{12} and $2\sigma^2 (2\pi/\mu m_{12})^{\frac{1}{2}}$. It is further assumed that f_{12} does not depend on the temperature, being a purely molecular property. Writing

$$\frac{dN_1}{dt} = \frac{dN_2}{dt} = -\kappa N_1 N_2$$

we can easily obtain the expression for κ , and on taking the logarithm we find it to be equal to the sum of the following seven expressions

$$\begin{aligned} & \log f_{12} \\ & \log \{2\sigma^2 2\pi/km_{12}\}^{\frac{1}{2}} \\ & \log \theta^{\frac{1}{2}} \\ & \log w_{1a} - \mu \epsilon_{1a} \\ & \log w_{2a} - \mu \epsilon_{2a} \\ & - \log \{w_{1n} \exp(-\mu \epsilon_{1n}) + w_{1a} \exp(-\mu \epsilon_{1a})\} \\ & - \log \{w_{2n} \exp(-\mu \epsilon_{2n}) + w_{2a} \exp(-\mu \epsilon_{2a})\} \end{aligned}$$

If we proceed to differentiate $\log \kappa$ with respect to θ , we find that the first two expressions above contribute nothing, and $d \log \kappa / d\theta$ is equal to the sum of five expressions

$$\begin{aligned} & \frac{1}{2\theta} \\ & \frac{\epsilon_{1a}}{k\theta^2} \\ & \frac{\epsilon_{2a}}{k\theta^2} \\ & - \frac{\epsilon_{1n} w_{1n} \exp(-\mu \epsilon_{1n}) + \epsilon_{1a} w_{1a} \exp(-\mu \epsilon_{1a})}{k\theta^2 \{w_{1n} \exp(-\mu \epsilon_{1n}) + w_{1a} \exp(-\mu \epsilon_{1a})\}} \end{aligned}$$

and a similar expression for type 2 molecules.

A little thought will show that the fourth of these is simply $-\epsilon_{1m}/k\theta^2$, where ϵ_{1m} is the *average* energy of all the molecules of type 1. In effect, ϵ_{1m} is but little different from ϵ_{1n} , if the latter is much less than ϵ_{1a} .

To sum up, we find that

$$\begin{aligned} \frac{d \log \kappa}{d\theta} &= \frac{1}{2\theta} + \frac{(\epsilon_{1a} + \epsilon_{2a}) - (\epsilon_{1m} + \epsilon_{2m})}{k\theta^2} \\ &= \frac{\zeta + \frac{1}{2}k\theta}{k\theta^2} \end{aligned}$$

where ζ is written for $(\epsilon_{1a} + \epsilon_{2a}) - (\epsilon_{1m} + \epsilon_{2m})$, *i.e.*, the amount by which the combined internal energies of the activated molecules exceeds their combined energies in the average state, or practically in the lower quantum unactivated state. This clearly corresponds to Arrhenius' "energy of activation," or as it is sometimes called the "critical increment" of energy. Practically $\frac{1}{2}k\theta$ is insignificant compared to ζ , and we obtain Arrhenius' well-known equation

$$\frac{d \log \kappa}{d\theta} = \frac{\zeta}{k\theta^2} \quad . \quad . \quad . \quad . \quad (III. 3)$$

or

$$\frac{d\kappa}{d\theta} = \kappa \frac{\zeta}{k\theta^2}$$

As is easily shown, this is quite consistent with the very rapid increase of κ with temperature. Indeed (III. 3) is

used in connection with the experimental determinations of κ over wide ranges of temperature to determine the value of ζ . For details the reader is once more referred to texts of Physical Chemistry.

Despite the rather clumsy appearance of the mathematical expressions involved, and the still more complicated expressions employed if we had used several upper quantum states instead of one, the Arrhenius result is essentially dependent on the factors of the type $e^{-\mu}$ in the formulæ for the numbers of activated molecules, and it is apparently very satisfactory that the result should follow so directly from this universal characteristic of statistical formulæ. But there is a very important feature of the treatment which has to be dealt with, and which has in certain cases presented very serious difficulties.

The reaction removes the activated molecules from the original system; they form molecules of the resultant substances in an upper quantum state; their excess energy is lost in subsequent collisions (presumably), and they become resultants in a normal state, the algebraic difference between the energy of activation and the excess energy of resultants subsequently lost being the ordinary heat of reaction (positive or negative) per molecular group. Of course, we know that among the remaining unactivated molecules a redistribution of internal energies would take place, leading once more to the usual statistical arrangement, *provided the chemical reaction did not go on*. It is clear, therefore, that in order to use *equilibrium* formulæ, even for approximate calculations, we must be satisfied that the reaction goes so slowly that there is always in existence a group of activated molecules not too small in number compared with the equilibrium number, and that implies that the rate of production of activated molecules is at least equal to the rate at which they are removed by the reaction. Here, then, we are faced with a problem of mechanism. We know that the system when denuded of activated molecules will proceed to make them good. But will it proceed at a fast enough rate? Mechanisms differ, as we pointed out above, not in their ultimate goal, but in the rate

degree, this gives 22,000 as the value for ζ/k . The reaction has been studied over the range 550° K to 780° K; so, putting θ as approximately 600, we see that $\mu\zeta$ (*i.e.*, $\zeta/k\theta$) is over 30, and in comparison unity is negligible in the second factor of (III. 4). The formula for C is given in (I. 4), and so the rate of collision for molecules with relative kinetic energy above ζ is practically

$$N^2 \sigma^2 \left(\frac{4\pi}{mk} \right)^{\frac{1}{2}} \theta^{-\frac{1}{2}} \zeta \exp(-\mu\zeta) \quad . \quad . \quad . \quad \text{(III. 5)}$$

In this we can put $\sigma = 2 \times 10^{-8}$, $m = 210 \times 10^{-24}$, $k = 1.35 \times 10^{-16}$, $\zeta/k = 22,000$, $\theta = 600$, $N = 6 \times 10^{20}$ (*i.e.*, a concentration of 1 gram-molecule per litre). The result is approximately

$$2 \times 10^{14}$$

On the other hand, the observed rate of reaction shows that about

$$2 \times 10^{13}$$

molecules of HI (at a concentration of 1 gram-molecule per litre and a temperature, 600° K) react per second. So there would appear to be a "factor of safety" of about 10, which does not appear to be too much to spare, since only a favourably circumstanced fraction of the 2×10^{14} collisions per second can result in activation. But we must not overlook one assumption which we are implicitly making at the moment. It is that all the spare kinetic energy is going into *one* of the colliding molecules, or that about one-tenth of all the collisions worth considering result each in one activated molecule. Indeed, the treatment so far is tantamount to assuming that one-tenth of a certain group of suitable collisions result at once in the reaction; for a little thought will show that the intermediate state of activation and subsequent collision between two activated molecules, each one arising from a different collision, is an unnecessary part of the picture as we have been treating it so far. Indeed, if we consider such a simple collision theory of reaction in which activation is not required (or at most is merged

into the process of collision), we can write for the rate of reaction

$$N^2 \propto \sigma^2 \left(\frac{4\pi}{mk} \right)^{\frac{1}{2}} \theta^{-\frac{1}{2}} \zeta \exp(-\mu\zeta) \quad . \quad . \quad . \quad (\text{III. } 6)$$

where α is an average value for the fraction of collisions which result in reaction. As matters stand now, we would have to take about 1/10 for the value of α in the case of hydrogen iodide, and, in other cases, the fraction does not appear to be any less. However, there are other considerations bearing on internal energy which tend to show this *simple collision* theory of reaction in a more favourable light. Before considering these, however, let us glance for a moment at a more genuine *activation* theory, *i.e.*, one in which collisions leading to activation and collisions of activated molecules leading to reaction are distinct occurrences.

Looking back to our earlier expressions, we see that the energy of activation is the sum of $\epsilon_{1a} - \epsilon_{1m}$ and $\epsilon_{2a} - \epsilon_{2m}$, so that it is not necessary to assume that an activating collision must give to either of the molecules the whole of the energy of activation. In the case of hydrogen iodide, for instance, an activating collision is only required to give one of the molecules engaging in it half the energy of activation; in a subsequent collision with another molecule activated with the half amount, the total amount is then presumably available for the splitting into H_2 and I_2 . This means that in using (III. 5) for the calculation of the upper limit of the number of collisions which might result in activation, we do not write $\exp(-22,000/\theta)$ for $\exp(-\mu\zeta)$, but $\exp(-11,000/\theta)$, which is practically ϵ^{18} times as great, and this certainly offers an ample margin for favourable collisions.

Thus, while there is a good deal to be said on statistical grounds for a theory which would consider that bimolecular reactions occur through the collisions of *previously* activated molecules, there must be an element of doubt about a simple collision theory in which we would assume that normal molecules can react at once if they collide with sufficient relative velocity. Indeed, if we calculate, as Tolman does, on a more stringent basis, which assumes that the kinetic

energy corresponding to the *resolved component* of the relative velocity along the line of centres is the only available source for the reaction, then even the factor of safety of 10 or thereabouts disappears, and we have, in general, just a rough equality between rate of reaction and rate of favourable collisions.

However, on other grounds, the theory of activation does not seem to be in such favour nowadays among physical chemists, and R. N. Fowler has pointed out that the simple collision theory can be rendered much more plausible by introducing available internal energy considerations, as well as merely available relative kinetic energy. In deriving Arrhenius' expression, we assumed for simplicity of writing just two quantum states, a normal and an activated; but it is much more probable that in reality there are a number of quantum states between the normal and the activated. Hence, in considering collisions with a definite relative kinetic energy, we can assume that some of these will be between molecules whose internal states, while not high enough for activation, are not as low as the normal. These would contain internal energy available for reaction purposes, and would obviously allow us to put the necessary amount of relative kinetic energy at a lower figure than before, and, in effect, bring into the favourable field many collisions previously ruled out. To render the necessary mathematical analysis which develops this idea as simple as possible, we will revert to the picture of internal harmonic oscillators as the seat of this internal energy, and carry out the calculations along classical lines. The internal energy is (for f oscillators)

$$\sum_{r=1}^f \left(\frac{p_r^2}{2a_r} + b_r q_r^2 \right).$$

If we wish to calculate the number of molecules whose internal energy lies between η and $\eta + \delta\eta$, we must integrate

$$\exp \left\{ -\mu \left[\frac{p_1^2}{2a_1} + b_1 q_1^2 + \dots \right] \right\} dq_1 \dots dp_f$$

for all values of $q_1 \dots p_f$ which correspond to

$$\eta + \delta\eta > \frac{p_1^2}{2a_1} + \dots + b q_f^2 > \eta$$

divide the result by the same integral over all values of q_1, \dots, p_f , and multiply by N . The method of carrying out such integrations as occur in the numerator is associated with the name of Dirichlet, and will be found in standard texts of mathematical analysis.* The result sought for is known to be

$$N \frac{\eta^{f-1} \exp(-\mu \eta) \delta \eta}{\int_0^\infty x^{f-1} \exp(-\mu x) dx}$$

The denominator is, of course, equal to

$$\frac{1}{\mu^f} \int_0^\infty y^{f-1} \exp(-y) dy$$

and the integral is known to be equal to $(f-1)!$

Hence the number of molecules whose internal energy lies between η and $\eta + \delta\eta$ is

$$\frac{N \mu^f}{(f-1)!} \eta^{f-1} \exp(-\mu \eta) \delta \eta \quad . \quad . \quad \text{(III. 7)}$$

Using (I. 7) and (III. 7), we can now calculate the number of collisions per unit volume per unit time between molecules of type 1 with internal energy between η_1 and $\eta_1 + \delta\eta_1$, and molecules of type 2 with internal energy between η_2 and $\eta_2 + \delta\eta_2$, the relative kinetic energy being between ξ and $\xi + \delta\xi$. It is the product of

$$2 \sigma^2 \left(\frac{2\pi\mu^3}{m_{12}} \right)^{\frac{1}{2}} \exp(-\mu\xi) \xi \delta \xi$$

and two expressions of the form (III. 7). The result is

$$\frac{2 \sigma^2 N_1 N_2}{(f_1-1)! (f_2-1)!} \left(\frac{2\pi}{m_{12}} \right)^{\frac{1}{2}} \mu^{f_1+f_2+\frac{1}{2}} \eta_1^{f_1-1} \eta_2^{f_2-1} \xi \exp[-\mu(\eta_1 + \eta_2 + \xi)] \delta \eta_1, \delta \eta_2, \delta \xi$$

To calculate the number of collisions for which the energy available for reaction purposes, viz., $\eta_1 + \eta_2 + \xi$, is greater than an assigned value ζ we must integrate this expression for

* Whittaker and Watson's *Modern Analysis* (3rd Edition), p. 238.

all values of η_1, η_2, ξ , satisfying this condition. Dirichlet's method is once more used, and yields the result

$$\frac{2 \sigma^2 N_1 N_2}{(f_1 + f_2 + 1)!} \left(\frac{2\pi}{m_{12}} \right)^{\frac{1}{2}} \mu^{f_1 + f_2 + \frac{1}{2}} \int_{\zeta}^{\infty} x^{f_1 + f_2 + 1} e^{-\mu x} dx$$

which is equal to

$$\frac{2 \sigma^2 N_1 N_2}{(f_1 + f_2 + 1)!} \left(\frac{2\pi}{\mu m_{12}} \right)^{\frac{1}{2}} \int_{\mu \zeta}^{\infty} y^{f_1 + f_2 + 1} e^{-y} dy$$

If $\mu \zeta$, or $\zeta/k\theta$ is sufficiently large, this is equal to

$$\frac{2 \sigma^2 N_1 N_2}{(f_1 + f_2 + 1)!} \left(\frac{2\pi}{\mu m_{12}} \right)^{\frac{1}{2}} (\mu \zeta)^{f_1 + f_2 + 1} e^{-\mu \zeta}.$$

If the molecules are of one type the factor 2 must as usual be removed, and we obtain

$$\sigma^2 N^2 \left(\frac{4\pi}{\mu m} \right)^{\frac{1}{2}} \frac{(\mu \zeta)^{2f+1}}{(2f+1)!} \exp(-\mu \zeta) \quad . \quad (\text{III. } 8)$$

Let us assume then that (III. 8) gives the law of reaction κN^2 , where

$$\kappa = \alpha \sigma^2 \left(\frac{4\pi}{\mu m} \right)^{\frac{1}{2}} \frac{(\mu \zeta)^{2f+1}}{(2f+1)!} \exp(-\mu \zeta)$$

α being some fraction giving on the average the relative number of sufficiently energetic collisions which result in a reaction; then, taking the logarithm of κ and differentiating, we find

$$\begin{aligned} \frac{d \log \kappa}{d \theta} &= \frac{\zeta}{k \theta^2} - \frac{2f + \frac{1}{2}}{\theta} \\ &= \frac{\zeta - (2f + \frac{1}{2}) k \theta}{k \theta^2} \end{aligned}$$

But, experimentally, we find the energy of activation from the Arrhenius formula

$$\frac{d \log \kappa}{d \theta} = \frac{\zeta_e}{k \theta^2},$$

where ζ_e indicates the experimental value of the energy of activation as distinct from ζ , which represents the lower limit of the theoretical available energy.

Hence

$$\zeta_e = \zeta - (2f + \frac{1}{2}) k \theta$$

and so (III. 8) becomes, in terms of the experimentally determined energy of activation,

$$\sigma^2 N^2 \left(\frac{4\pi}{\mu m} \right)^{\frac{1}{2}} \frac{(\mu \zeta_e + 2f + \frac{1}{2})}{(2f + 1)!} \exp(-[\mu \zeta_e + 2f + \frac{1}{2}]) \quad (\text{III. 9})$$

while (III. 5) becomes

$$\sigma^2 N^2 \left(\frac{4\pi}{\mu m} \right)^{\frac{1}{2}} (\mu \zeta_e + \frac{1}{2}) \exp(-[\mu \zeta_e + \frac{1}{2}]). \quad (\text{III. 10})$$

which is just (III. 9) when f is made zero.

Now (III. 9) bears to (III. 10) a ratio which is practically

$$\frac{(\mu \zeta_e)^{2f}}{(2f + 1)!} e^{-2f}$$

an expression which may easily be greater than unity. Thus, for hydrogen iodide, f is at least unity, and the ratio becomes if that value is assumed

$$\frac{1}{6} \left(\frac{\zeta_e}{k \theta} \right)^2 e^{-2}.$$

As ζ_e is more than thirty times as great as $k\theta$ in this case, this ratio is about 20, and it follows that to meet the experimental rate of reaction, the simple collision theory, if supplemented by this hypothesis of internal available energy, would only require α to have on the average a value about 1/200, which leaves a very good margin indeed.

On statistical grounds, then, the collision theory of bimolecular homogeneous gas reactions can be regarded in a favourable light. It is, however, a well-known fact that serious difficulty has hitherto attended similar considerations when applied to reactions of the first order in which the rate of reaction is proportional to the first power of concentration and not to its square, the best discussed example being the decomposition of nitrogen pentoxide. We can, of course, as before, assume that the molecules entering into reaction have been previously activated by collision, but it is hard to admit that reaction is due to collision of activated molecules, since the rate of reaction would surely be proportional to

square of concentration and not to first power. In order to evade this difficulty, it is generally assumed that once a molecule has been activated, there is a definite chance that before it can be deactivated by another collision, it will spontaneously disintegrate. That is, collisions leading now to activation and now to deactivation, maintain an equilibrium distribution in the usual statistical manner between the normal and various quantum states (including the activated state) or nearly so, for combined with this is this postulated disintegration mechanism which tends to upset this distribution (but not too rapidly) by denuding the system of its activated molecules. Since the concentration of activated molecules is proportional to $\exp(-\mu\epsilon_a)$, it follows that the number of activated molecules at any moment is

$$N \frac{w_a \exp(-\mu\epsilon_a)}{w_n \exp(-\mu\epsilon_n) + w_a \exp(-\mu\epsilon_a)},$$

and remains practically unaffected if the rate of reaction is slow enough; as there is a definite chance that such a molecule will disintegrate before another collision tends to deactivate it, this rate of reaction will be proportional to the expression just written and so to the first power of N . Moreover, κ will be equal to

$$A \frac{w_a \exp(-\mu\epsilon_a)}{w_n \exp(-\mu\epsilon_n) + w_a \exp(-\mu\epsilon_a)}$$

where A is a constant *independent of the temperature*. Taking the logarithm and differentiating with respect to θ , we find just as before Arrhenius' equation

$$\frac{d \log \kappa}{d \theta} = \frac{\zeta}{k \theta^2}$$

where $\zeta = \epsilon_a - \epsilon_n$, or practically $\epsilon_a - \epsilon_n$.

This picture of the occurrence is due to Lindemann (*Trans. Faraday Soc.*, Vol. 17, p. 599 [1921]). The difficulties attending it have as usual centred round the necessity of finding the rate of activation to be fast enough. It is impossible in this short appendix to go into the matter at any length. The case of nitrogen pentoxide proves to be the most refractory. Thus if activation had only relative

movement to look to for its energy, it can be shown that it would take place at a rate about .0001 of that required. That is Tolman's view, using his very stringent formula involving relative motion resolved along the line of centres as the only effective source of energy of activation. (See Tolman's *Statistical Mechanics*, Chapter XXI., section 326.) To be sure, if the full relative motion is considered, matters do not look so bad, and, as Fowler shows, if we supplement the energy of relative motion with internal energy, using a reasonable number of internal degrees of freedom, we can just bring the case of nitrogen pentoxide within the bounds of possibility without anything to spare, however; moreover, there are three or four other unimolecular gaseous reactions which are well within the grasp of Lindemann's hypothesis, as amplified by Fowler, without making too great demands on the probabilities of the situation. (For details, consult Fowler's *Statistical Mechanics*, Chapter XVII. section 4.)

Apart from Fowler's considerations, however, and indeed some years before he advanced them, Christiansen and Kramers (*Zeitschrift für physik. Chem.*, Vol. 104, p. 451 [1923]) attempted to meet the difficulty of Lindemann's hypothesis by pointing out that the resultants of the decomposition would contain energy above the normal; such energy must leave them when becoming normal resultant molecules, and it seems natural to look for the cause of this loss in ordinary collisions which convert this energy into heat motion of the molecules. But these authors suggest that this energy might be used at all events in part for activation purposes. In short, activated molecules of the resultants will collide with unactivated molecules of the reactant and transfer this energy as internal energy to the latter, little or none of it transforming into translatory kinetic energy. The difficulties attending this hypothesis are discussed by Tolman in the reference cited above.

Finally, it remains to refer briefly to another theory of activation propounded nearly fifteen years ago by W. C. Lewis, and independently about the same time by Perrin. A full account of it will be found in Lewis's *System of Physical*

Chemistry, Vol. III., Chapter VII. It looks for the energy of activation, not to collisions but to the thermal radiation surrounding the reacting molecules, and in temperature equilibrium with the walls of the enclosing vessel. It assumes that a molecule to become active absorbs a quantum of energy whose frequency corresponds to the value given by the equation, energy of activation = $h\nu$. If one uses the expressions for rate of absorption of radiation developed in the Planck theory of full radiation, however, this hypothesis finds itself in as bad, if not a worse, situation as regards nitrogen pentoxide than the simple collision theory of activation. The advantage of it is that it gives a simple explanation of the unimolecular nature of the reaction without resort to hypotheses of spontaneous disintegration. As regards bimolecular reactions, the radiation theory is quite satisfactory if it is assumed that the radiation has only to supply a portion (say one-half) of necessary energy of activation to one molecule and the remaining portion to the other, collisions between previously activated molecules producing the reaction. This radiation theory seems to have receded into the background lately, although Tolman in his book discusses it in a very favourable way, showing how an elaboration of it may be possibly made to fit the facts. The author had many private discussions on this matter with Professor Lewis some years ago, and has attempted to present the simple radiation theory in a form which yields a criterion distinguishing molecules engaging in unimolecular reactions from those engaging in bimolecular and at the same time suggests a possible escape from the rate of activation difficulty (Rice, "Note on the Radiation Theory of Chemical Reaction," *Trans. Faraday Soc.*, No. 63, Vol. XXI., Part 3). Any reader with a sufficient knowledge of electromagnetic theory could follow the argument advanced in this note, but the author must point out that his reasoning leads to an abnormal reflecting power of nitrogen peroxide for radiation of the activating frequency which would be just below the visible red, and some unpublished observations carried out by E. A. Stewardson at the author's request do not confirm this.

As matters stand now, it would appear that a collision mechanism is the least unsatisfactory hypothesis for activation. It is quite possible, in view of the solution of similar difficulties of quantum states in other processes by the New Mechanics, that the theory of activation, if it survives, will look in this direction for a better formulation.

As regards the application of the formulæ of Section I. to the treatment of viscosity and diffusion in gases, the reader will find a sufficiently elementary account in the English translation of Bloch's *Kinetic Theory of Gases* (published by Methuen), and in view of the elegant and simple treatment to be found in Chapter III. of that little volume, there appears to be no need to continue this appendix further.

NOTE ON CHAPTER X

The Smoluchowski formula used in connection with fluctuations was derived in Chapter X. from a rather detailed consideration of the circumstances, so as to make the argument as concrete as possible to the beginner. It can, however, be derived in a more abstract fashion by a method due to Einstein.

Consider the normal state of a system in which the internal energy is U and the free energy F , so that

$$F = U - \theta S$$

where S is the entropy, or

$$S = \frac{U - F}{\theta}.$$

Indicate a state to which the system can fluctuate by primed symbols, the internal energy and temperature still being the same however. Let this state be one to which the system could be brought from the normal by external work of amount δE performed on the system. Then since

$$\delta F = - S \delta \theta + \delta E$$

and $\delta \theta$ is zero, it follows that

$$F' = F + \delta E$$

and

$$\begin{aligned} S' &= \frac{U - F' - \delta E}{\theta} \\ &= S - \frac{\delta E}{\theta} \end{aligned}$$

But

$$S = k \log W$$

and

$$S' = k \log W'$$

by Boltzmann's formula. Hence

$$\frac{W'}{W} = \exp \left(\frac{S' - S}{k} \right)$$

or
$$W' = W \exp \left(\frac{-\delta E}{\theta} \right)$$

which is Einstein's general formula. In Chapter X.

$$\delta E = - \int_{v_0}^{v_r} (p - p_0) dv$$

and Smoluchowski's result follows.

SUGGESTIONS FOR FURTHER READING

THOSE readers who wish to pursue the subject further mainly for its applications in Physics and Chemistry will find an excellent guide in R. C. Tolman's "Statistical Mechanics" (American Chemical Society Monograph Series, published by the Chemical Catalog Company, New York). The recently published "Statistical Mechanics" of R. H. Fowler is a very exhaustive treatise and, for those who possess sufficient mathematical equipment, a veritable mine of information on the many topics, physical, chemical and astrophysical, to which the statistical method can be applied. It is published by the Cambridge University Press. These books give numerous references to the original literature.

The classical work is, of course, Willard Gibbs' "Elementary Principles in Statistical Mechanics" (Yale University Press). Based on the treatment of ensembles of similar dynamical systems its "modest aim," in the words of its author, is that "of deducing the more obvious propositions relating to the statistical branch of mechanics." It does not in the main concern itself with thermodynamic phenomena or with the "mysteries of Nature," confining itself to logical deduction without reference to hypotheses concerning the constitution of matter. Nevertheless, no serious student of the subject should fail to read it, and its four last chapters do at all events discuss the relations of the subject to natural phenomena with that insight for which the author was so justly famous.

A very important monograph by P. and T. Ehrenfest discusses the origin of the subject and the gradual clarification of its fundamental postulates. Its title is "Begriffliche Grundlagen der statistischen Auffassung in der Mechanik."

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It is Heft 6 of Band IV. 2 II. of the "Encyclopädie der Mathematischen Wissenschaften."

There are several works on the applications of the statistical method to gases. The book for those whose time and mathematical knowledge are limited is E. Bloch's "Kinetic Theory of Gases," a translation of which is published by Methuen. The standard works are, of course, Boltzmann's "Vorlesungen über Gastheorie," and Jeans' "Dynamical Theory of Gases." An American work, "Kinetic Theory of Gases," by Loeb (Published by Ginn & Co.), combines the usual theoretical treatment with useful accounts of recent experimental research on gases.

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